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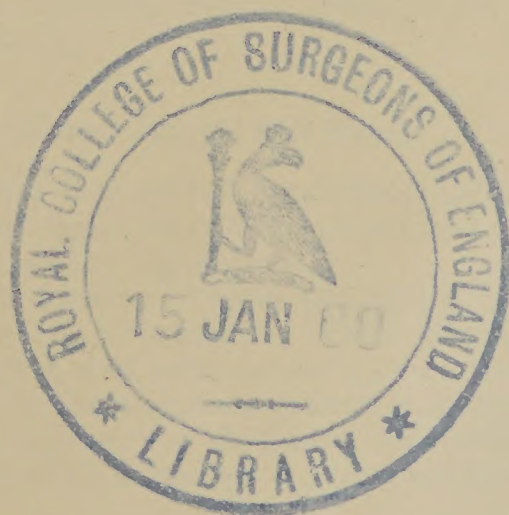
IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, F.R.S., &c.

VOLUME LXXX.—1899.



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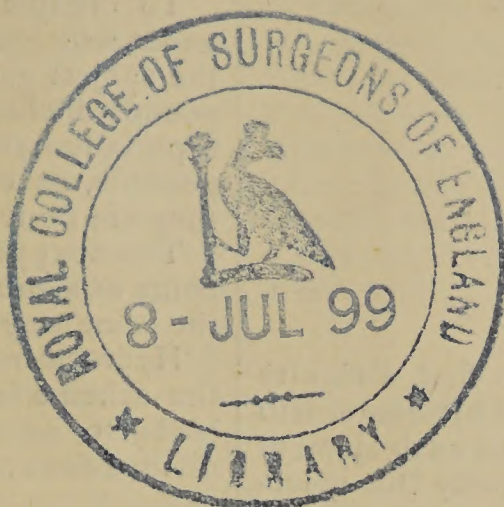
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VOLUME LXXX.

EDITED BY SIR WILLIAM CROOKES, F.R.S., &c.

No. 2067.—JULY 7, 1899.

THE CLASSIFICATION OF CHEMISTRY, AS PROPOSED BY THE COMMITTEE ON THE INTERNATIONAL CATALOGUE OF SCIENTIFIC LITERATURE.*

A CRITICAL ANALYSIS.

By H. CARRINGTON BOLTON
and
WILLIAM P. CUTLER.

If the object of arranging titles of books in a bibliography in certain groups or classes is to enable readers and investigators to find more readily an article on a given subject, then the *anonymous* Committee that drew up the schedule of classification for Chemistry in the Report of the Royal Society's International Catalogue Committee has made an almost total failure.

Two methods were open to the Committee appointed to devise a classification scheme for Chemistry, either to adopt an arbitrary system, in which symbols uniformly indicate definite subjects, or to adopt the dictionary plan, in which specific words are arranged alphabetically. The latter plan has, in our opinion, great and incontestable advantages over the former, but as the Committee chose to adopt the first named method the second cannot be here considered.

The provisional plan which was submitted to the delegates at the Conference of the International Catalogue Committee, held in London, October, 1898, forms Section F, of the general scheme printed in a small volume, very difficult for others than delegates to obtain. The grand divisions, with their registration symbols, are as follows:—

(No number) Chemical Bibliography.

0100 Chemistry (Specific) of the Elements.

0900 Laboratory Procedure.

1000 Organic (Carbon) Chemistry (Specific).

1010 Hydrocarbons.

1100 Alcohols and Ethers.

1200 Acids.

1300 Aldehydes and Ketones.

1400 Carbohydrates; Glucosides; Resins.

1500 Amino- and Azo-Compounds.

1600 Mixed Cycloids.

1700 Organo-Metallic and Allied Compounds.

1800 Alkaloids.

1900 Proteids.

2000 Coloured Compounds.

2500 Operations in Organic Chemistry.

3000 Analytical Chemistry.

3500 Theoretical and Physical Chemistry.

4000 Physiological Chemistry.

These grand divisions are sub-divided so as to provide a class and a symbol for every substance known to the chemist or awaiting discovery; at least such is the intention. Chemical Bibliography is divided into six groups, to wit:—

0000 Philosophy.

0010 History.

0020 Biography.

0030 Dictionaries, collected works, monographs, and text-books.

0040 Pedagogy.

0050 Addresses, lectures, essays, and theses.

Curiously, no symbol is provided for bibliographies of chemistry, a topic that must have been prominent in the minds of the persons on the Committee.

The second grand division "0100 Chemistry of the Elements" is intended to embrace "all specifically chemical subject-matter, and such other entries as may be desirable, relating to the elements generally, excepting carbon." In this category the elements are arranged alphabetically, and to each a symbol is given, thus:—

0110 (Al) Aluminium.

0120 (Sb) Antimony.

0130 (A) Argon.

* * *

0200 (Cd) Cadmium,

0210 (Cs) Cæsium.

* * *

* Advance proofs from *Science*, June, 1899.

0250 (Cl) Chlorine.
0260 (Cr) Chromium.
* * *
0800 (Va) Vanadium.
0810 (Yt) Ytterbium.
0820 (Y) Yttrium.
0830 (Zn) Zinc.
0840 (Zr) Zirconium.

Students, and even older chemists, who find difficulty in recalling the atomic weights of common elements, will scarcely welcome the proposition to give to each element another factor, though in the case of antimony this objection disappears.

This alphabetical arrangement of the elements prevents carrying out one of the prime objects of classification, namely, the grouping of related matters; thus—

0270 = Cobalt, 0500 = Nickel,
0690 = Sulphur, 0710 = Tellurium.

The natural group Ba, Ca, and Sr have respectively the unrelated numbers 0150, 0220, and 0680. Surely the elements might have been arranged systematically, so that related bodies would have contiguous symbols.

Annexed to the table of elements are instructions for sub-dividing entries and the following paragraph:—"Specific entries relating to the halogens collectively shall be arranged in Division 0250 under *Halogens*." This mixing of a word-heading with numerical symbols is a weak feature to be again noticed.

The instructions for entering titles in sub-divisions of 0100 include the following paragraph:—"Entries relating to compounds, which in the Slip Catalogue bear the number and symbol of the dominant element, together with the symbol of the secondary constituent, or dominant second constituent, shall be printed in the sub-division of their second constituent." If we understand aright this rather obscure sentence, it provides for writing on slips according to one rule and for printing them in book form according to another rule; sodium chloride would appear, therefore, under the symbol for sodium in the written slips and under chlorine in the printed volume!

A second paragraph provides that "references to hydroxides, acids, and salts shall be entered under the oxide, and corresponding sulphur compounds under the sulphide."

A third paragraph reads as follows:—"(*d*) In each sub-division the entries shall be arranged in such order that those relating, *a*, to the history or origin of the substance come first, and following these, in the order mentioned, those relating, *β*, to its preparation or manufacture; *γ*, to its structure, or of a theoretical nature; *δ*, to its interactions or use; *ε*, to its compounds—these five several sections being denoted by the letters *a*, *β*, *γ*, *δ*, *ε*."

Passing without comment this non-parsable English (which occurs elsewhere in the report), the scheme introduces another arbitrary feature, Greek letters for specific subjects, which is an admission that the numerical plan is found insufficient; though it need not be, provided decimals were used, a plan which does not seem to be contemplated by the Committee. The suggestion is even made that "it would be possible to carry the analysis still farther by means of symbols, such as *ψ*, *κ*, and so forth, to indicate physical properties, crystalline form, &c." The writers of this review venture to suggest that when the Greek alphabet is exhausted the Hebrew will come in handy.

This mixture of numerical symbols with word-headings is again resorted to in division "0930 Operations in Inorganic Chemistry," where it is suggested that "entries shall be made under significant headings, such as dissolution (*sic*) and solvents, crystallisation, distillation, . . . oxidation, electrolysis, furnace operations, &c., arranged alphabetically."

To organic chemistry the symbol 1000 is assigned, under which all entries shall be arranged that relate to the subject generally; substitution derivatives of the compounds included in each of the numbered divisions—especially haloid and allied derivatives—shall, as far as possible, be entered under the compounds from which they are derived.

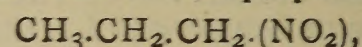
The next paragraph provides that "entries under the name of a substance may, if necessary, be sub-divided in the same way as that proposed for inorganic substances."

Hydrocarbons receive the numerical symbol 1010, and the scheme for indicating their substitution derivatives, leads to amazing propositions; the general group is divided thus:—

1010 Hydrocarbons.
1020 Paraffins.
1030 Unsaturated Open-chain Hydrocarbons.
1040 Benzenoid Hydrocarbons.
1050 Reduced Benzenoid Hydrocarbons (Terpenes, &c.).
1060 Unclassified Hydrocarbons.

"Each of these divisions shall be sub-divided (excepting 1010 and 1020) into isologous groups, in each of which compounds shall be entered in homologous order. Then follow two new arbitrary signs for distinguishing derivatives; these are full-faced numerals, 2, 4, &c., used to indicate homologous series C_nH_{2n-2} , C_nH_{2n-4} , and the full-faced letter C, with exponents attached, to indicate the number of carbon atoms in a given compound.

Applying this scheme to nitropropane,—



it will receive the registration symbol 1020.C₃.NO₂; allene, C₂:C:CH₂, will be indicated by the symbol 1030.2.C₃, and bromotoluene, C₆H₅.CH₂.Br, will be indicated by 1040.6.C₇.Br.

This plan of assigning to definite chemical bodies arbitrary symbols resembling in structure well-established formulæ is most objectionable; if carried out it would prove vexatious to chemists and of no practical value to librarians.

To alcohols and ethers the symbol 1100 is assigned; to acids, 1200; each of these groups is sub divided exactly as are the hydrocarbons, but the symbols of the sub-divisions do not harmonise. Since paraffins = 1020, "ols should have been 1120, and acids 1220 (instead of 1110 and 1210).

In the paragraph on acids, provision is made for indicating the number of oxygen atoms, the character of the acid, and the basicity by numbers, to which ol, al, on, id, or cy shall be appended, according to the origin of the acid. "Thus lactic acid would be marked 1210.C₃O₃ (1.01), and protocatechuic acid 1230.8.C₇O₄ (1.2.01)." Here, again, we have registration symbols resembling in a general way chemical formulæ, yet they do not show the constitution nor even suggest the name of the substance.

Number 1440 is given to carbohydrates other than mono-, di-, and trisaccharides, and 1450 to glucosides, and 1460 to resins, and it is provided that compounds belonging to these divisions shall be entered alphabetically; this is again a departure from the numerical plan. Another rule provides that "under alkaloids (1800) a list shall be given of vegeto-alkaloids, together with the Latin names of the plants from which they have been obtained, arranged in the alphabetical order of the plant names." Chemists not versed in botany would find this arrangement a puzzling one. Again, "alkaloids derived from plants (1810) and from animals (1820) shall be arranged alphabetically."

Division 2000 is styled "Coloured compounds" [1], a singular misnomer for compounds used in dyeing; yet another division, 2010, is called "Coloured substances, not dye-stuffs," and division 2020 is named "dye-stuffs." Provision is made for sub-dividing these categories thus:—

"2010 into Hydrocarbons (coloured), Alcohols (coloured), Ketones (coloured), &c.; 2020 into Azo dyes . . . dye-stuffs of vegetable origin, unclassified dyes," arranged alphabetically in each sub-division.

The rules concerning the entries of the sub-divisions of 3000, Analytical Chemistry, also lack uniformity, clearness, and exactness; "division 3200 shall include all entries relating to the determination of individual elements in their compounds and in mixtures, excluding determinations of atomic weights" which belong to division 3500 (theoretical and physical chemistry). Division 3300 shall include all entries relating to the determination of individual compounds, e.g., alkaloids, carbohydrates . . . but excluding gases. If necessary gravimetric, volumetric, electrolytic, physical, &c., methods may be distinguished by letters, such as *g*, *v*, &c." "Division 3400 (Applied Analysis) shall include all entries relating to the analysis of composite materials, such as drugs, foods, soils, waters, and technical products generally, arranged under appropriate significant headings."

The remaining divisions, 3500, Theoretical and Physical Chemistry, and 4000, Physiological Chemistry, must be passed; the specimens given are sufficiently numerous.

A study of this remarkable scheme of classification shows that the Committee failed to recognise the fact that classification and notation are two distinct things, and that a notation need have no relation to the character of the class to which the notation is given. To differentiate the houses in a city, street and number are given; "120 Grand Avenue" suffices to distinguish a given house, and it is not necessary to construct a symbol indicating the number of stories, the number of windows, and the colour of the paint in order to recognise the address.

Accompanying the schedule of classification is a specimen page giving illustrations of the way in which these rules should be applied; the examples bring out forcibly the absurdities of the conglomerate method proposed. The paper on Argon, by Lord Rayleigh and W. Ramsay, receives the kabbalistic formula "0100.β.φ," but if we understand rightly the Committee's rules, the numerals should be 0130, which stands for argon.

An article by J. J. Sudborough and L. L. Lloyd, on "Stereoisomerism as affecting formation of etheral salts from unsaturated acids," is assigned simply the number 3500; when, however, the same paper is entered under a different title, namely, "Etherification of stereoisomeric unsaturated acids a criterion of structure," it has the number 1200 γ; when, on the other hand, this paper is catalogued as: "Cinnamic and allied acids as a criterion of structure, Etherification of," the catalogue slip must bear the symbol 1230.10.C₉O₂δ.

To a chemist the formula of cinnamic acid C₆H₅.CH:CH₂.CO₂H has a definite meaning, and we protest against a system that introduces symbols, analogous in appearance, yet wholly misleading as respects the composition.

An examination of the schedule of classification of Chemistry proposed by the International Catalogue Committee shows that it consists of a medley of several methods. The system includes:—

1. Numbers, full-face, and inferiors, used for several distinct purposes.
2. Roman capitals, to denote component elements.
3. Roman lower-case, to denote kind of chemical process.
4. Italic letters in parenthesis, to denote basicity of acids.
5. Greek lower-case letters.
6. Word-headings arranged alphabetically.
7. Special provisions; exceptions to rules.

In 1772, at Ulm, was printed a thin octavo, having the title "Medicinisch-chymisch und alchemistisches oraculum," which contains a key to over two thousand symbols and kabbalistic figures found in alchemical manuscripts and books; the book is curious and instructive, as well as

really serviceable to antiquarian chemists. The number of synonyms for a given substance is large; alum has twenty-six; aqua fortis, twenty-two; mercury, thirty-eight; a pound weight, eight, and cream of tartar is credited with thirty-two; the symbols have an uncouth appearance, but are hardly more fanciful than those proposed by the Committee on the International Catalogue. Should their schedule of classification prevail, a new edition of the "Alchemical Oracle" would soon become a necessity.

THE PARENT-ROCK OF THE DIAMOND IN SOUTH AFRICA.*

By Professor T. G. BONNEY, D.Sc., LL.D., V.P.R.S.

So much has been written on the occurrence of diamonds in South Africa that a very few words may suffice as preface to this communication. References to many papers on the subject are given in "The Genesis and Matrix of the Diamond" (1897), by the late Professor H. Carvill Lewis,† and others have been published since that date.‡ It may suffice to say that the diamond, first discovered in 1867 in gravels on the Orange River, was found three years later in certain peculiar deposits, which occur locally in a region where the dominant rock is a dark shale, sometimes interbedded with hard grits, or associated with igneous rocks allied to basalt. These deposits occupy areas irregularly circular in outline, and bearing a general resemblance to volcanic necks. The diamantiferous material, near the surface, is soft, yellowish in colour, and obviously much decomposed; at a greater depth it assumes a dull greenish to bluish tint, and becomes harder. At the well-known De Beers Mine, near Kimberley, the works in 1898 had been carried to a depth of about 1500 feet, and the diamantiferous material, for at least the last 100 yards, was not less hard than an ordinary limestone. It has a brecciated aspect, the dark, very minutely granular, matrix being composed mainly of serpentine (about four-fifths of the whole), and of a carbonate of lime (with some magnesia and a little iron). In this matrix are embedded grains of the following minerals:—Olivine, enstatite, smaragdite, chrome-diopside (omphacite of some authors), a brown mica, garnet (mostly pyrope, but more than one variety observed), magnetite, chromite, ilmenite, with several other minerals much more sparsely distributed.

Rock fragments are also present, variable in size, but commonly not exceeding about an inch in diameter, as well as in quantity. These occasionally, but not generally, are rather abundant. In some cases they are chips of the neighbouring black shale, but in others they are greyish-coloured with a somewhat porcelainised aspect. The latter are generally sub-angular in form, and externally banded or bordered with a darker tint; crystalline rocks have also been noticed, though these appear to be far from common, such as granite, diorite, and varieties of eclogite.§ As to the genesis of the diamond, more than one opinion has been expressed. Professor Lewis regarded the matrix as a porphyritic form of peridotite, once a lava, now serpentinitised,|| in which the diamond had been formed by the action of the molten rock on some carbonaceous material (probably the Karoo shale). Others

* A Paper read before the Royal Society, June 1, 1899.

† Edited by the present writer.

‡ Jules Garnier, *Geol. Soc. South Africa Trans.*, 1897, p. 91; H. S. Harger, *ibid.*, p. 124. See also W. G. Atherstone, *ibid.*, 1896, p. 76; L. De Launay, *Compt. Rend.*, 1897, cxxv., 335. The last author, in "Les Diamants du Cap" (Paris, 1897) gives a very full account of the mines, but an even better one will be found in Max Bauer, "Edelsteinkunde" (Leipzig, 1896, p. 208).

§ A. W. Stelzner, "Sitzungsber. u. Abhandl. der Isis" (Dresden), 1893 (April), p. 71, calls attention to the fact that these show signs of attrition and that they range in size from a few cubic millimetres upwards, being sometimes large boulders. Among the materials (at Kimberley) he mentions both granite and eclogite.

|| For the rock itself he proposed the name "kimberlite."

regarded the matrix as a true breccia, comparing it with the agglomerates in volcanic rocks. But among the latter, some thought that the diamond had been produced *in situ* by the action of steam or hot water in a subsequent solfataric stage of the volcano, while others (including myself) held that it had been formed, like the garnets, pyroxenes, &c., in some deep-seated holocrystalline mass which had been shattered by explosions.*

The specimens which I am about to describe were obtained at the Newlands Mines, West Griqualand; from 40 to 42 miles from Kimberley, almost due N.W. Here the workmen occasionally came across well-rounded boulder-like masses of rather coarsely crystalline rock, studded with garnets, which are sometimes about a foot in diameter. Specimens of these were found or obtained by Mr. G. Trubenbach, the London manager of the Newlands Diamond Mine Company, during a visit to the mines in 1897. His interest had already been aroused by picking up a specimen, presently to be noticed, in which some small diamonds occurred, very closely associated with a garnet; so the boulders were brought back by him to England. On careful examination a small diamond was detected on the surface of one of these. On breaking the boulder others were revealed. The most interesting fragment was sent by Mr. Trubenbach to Sir W. Crookes, who showed it to me. Examination with a hand lens convinced me that the rock could not be a concretion of the "blue ground," but was truly holocrystalline and allied to the eclogites. Sir W. Crookes generously waived his own claim to study the specimen, and obtained for me permission from Mr. Trubenbach to have slices cut from it. I gladly take this opportunity of expressing my gratitude to both gentlemen; to Sir W. Crookes for allowing me to carry out this interesting investigation, and to Mr. Trubenbach for his great liberality in placing at my disposal a considerable suite of specimens (including other boulders) from the Newlands mines, and for the trouble which he has taken in affording me the necessary information.

Prior to the discovery, just mentioned, one or two instances had occurred at the De Beers Mine of a diamond apparently enclosed by or projecting into a pyrope. One such, the garnet being the size of a rather large pea, is in the collection at Freiberg (Saxony), to which it was presented in 1892.†

The specimen found by Mr. Trubenbach at the Newlands mine was a piece of blue ground, with a pyrope projecting from one angle. A small, apparently broken, diamond seems embedded at the top. The others (five) are well crystallised, two on one side, three almost in contact on the other. The pyrope (which has a kelyphite rim) seems to be indented by two, but to have once included the others, as they are in contact with the unaltered mineral. We were thus brought so far as to associate the diamond with the pyrope; though this proved no more than the presence of garnets in the parent rock of the diamond, and thus made the eclogite (already known to occur) highly probable, for, as observed by Professor R. Beck,‡ the specimen itself is blue ground. In confirmation of his statement I pulverised a fragment,§ and find that the powder corresponds with the matrix of the blue ground when similarly treated. The latest discoveries enable me to complete the chain of evidence.

Eclogite Boulders containing Diamonds.

The first named, that containing several diamonds, is a

* In other words, that the volcano (as occasionally has happened) had ejected little or no lava or scoria, discharging only steam and hot water, with shattered rock. This view is held by Max Bauer, in "Edelsteinkunde," p. 225, which, however, I had not seen when this paper was written.

† A. W. Stelzner, "Sitzungber. der Isis zu Dresden," 1893, s. 85, and R. Beck, *Zeitsch. f. Praktische Geologie*, 1898 (May, p. 163).

‡ *Ut supra*.

§ I could not advise Mr. Trubenbach to have a slice cut from the specimen, as I feared it might be injured, but he kindly detached a little fragment from the opposite end to that named above, which I have thus examined.

fragment (perhaps from a quarter to a third) of a boulder, which probably was ellipsoidal in shape, two of the axes being nearly equal and the third distinctly the longest. We may infer that it was rounded from a roughly rectangular block, since the curved surfaces are slightly flatter in the middle parts. The axial lengths in the fragment (prior to removing a piece from one end) were approximately 4 in. by 3 in. by 2 in. The rock is coarsely granular, apparently composed of two green-coloured minerals, one darker than the other (possibly only different states of a single mineral), and of rich resin-pink coloured garnets, varying in size from a hemp-seed to a pea, with slightly irregular distribution. The outer surface of the boulder, except for a very small "step" on one side, is smooth, the garnets barely, if at all, projecting. The latter are covered with a rather soft, dark skin, sometimes slightly thicker than the thumb nail, which often has partly fallen off. This, as can be seen on the broken surfaces, becomes less conspicuous in the inner part of the boulder, and is sometimes invisible to the unaided eye. Two small diamonds are exposed on the curved outer surface, one about half, the other about one-fifth of an inch from the edge of the cross fracture. On the latter surface, nearly an inch below the last named, three small diamonds appear to lie in a line touching one another, and near them are two others,* all four within a space about three-quarters of an inch square; an eighth diamond is about an inch and a half away (on the same face); a ninth, about one-fifth of an inch from the top edge; and a tenth occurs on the larger cross-fractured surface, but near to the edge of the other one. These diamonds are octahedra in form, generally with stepped faces—one, at least, apparently twinned—perfectly colourless, with brilliant lustre; the largest being quite 0.15 inch from apex to apex, the smallest not exceeding 0.05 inch. All seem to be embedded in the green part of the rock. As the outer part of the boulder looks rather more decomposed than the inner, I had a piece removed from one end, thus enabling me to study the mass to a depth of more than an inch from the surface, and examined a strip, about 4 inches long, in a series of five slices.

The late Professor Lewis has given, in the volume already mentioned, so full an account of the minerals which occur in the "blue ground," that it will be needless on the present occasion to do more than refer to his descriptions,† only calling attention to any variations in the mineral constituents and their association in these eclogites. These constituents are:—

1. (a) *Garnet* (Pyrope).—In the slice these appear a light tawny or yellowish red tint, retaining this tint (though much lighter) under the microscope.‡ They are generally clear, with frequent and irregular cracks, but are occasionally traversed by wavy bands of minute enclosures of a pale brown filmy mineral, which is rather irregular in outline, very feebly pleochroic, and gives with crossed nicols fairly bright polarisation tints. Similar minerals sometimes have formed along the cracks. They are probably mica, or possibly chlorite, and indicate incipient decomposition. The garnets towards the outside of the boulder, as already said, are enveloped in a "skin," and the microscope shows that it usually exists inside, though there it is thinner. In the former case it is generally browner in colour and more distinctly crystalline, corresponding in cleavage, pleochroism, &c., with a mica of the biotite group; in the latter it is greener and more filmy with an aggregate habit, and seems to project into the garnet. I regard it as due to decomposition, a form

* It is possible that these two form a twin crystal, but I think they are separate. As the point is unimportant, I have not attempted to clear away the matrix.

† We must also not forget the paper by Professor Maskelyne and Dr. Flight (*Quart. Journ. Geol. Soc.*, vol. xxx., p. 406), in which several of these minerals are described, analysed, and identified. In fact, the authors ascertained everything that was possible with the materials then obtainable.

‡ Unless it is expressly stated, the use of a 1-inch objective may be assumed.

of the well-known kelyphite rim, sometimes a mica, sometimes a chlorite, possibly now and then associated with a little minute hornblende. In a few cases a "rim" is brown in the outer part and green within. The constituents tend to a parallel rather than a radial grouping. The garnets occasionally contain minute branching root-like enclosures grouped in bands. Though these act on polarised light, I regard them as empty cavities, and attribute this to diffraction.

cracks, is often converted into a minutely granular to fibrous mineral, which gives a "dusty" aspect to that part of the crystal when viewed with transmitted light, and a whitish-green one with reflected light. This often terminates in a minutely acicular fringe, piercing the original diopside. Its grains occasionally are a little larger, showing a cleavage, dull green in colour, fairly pleochroic, and having the extinction of hornblende. A process of secondary change, as in uralite, is no doubt

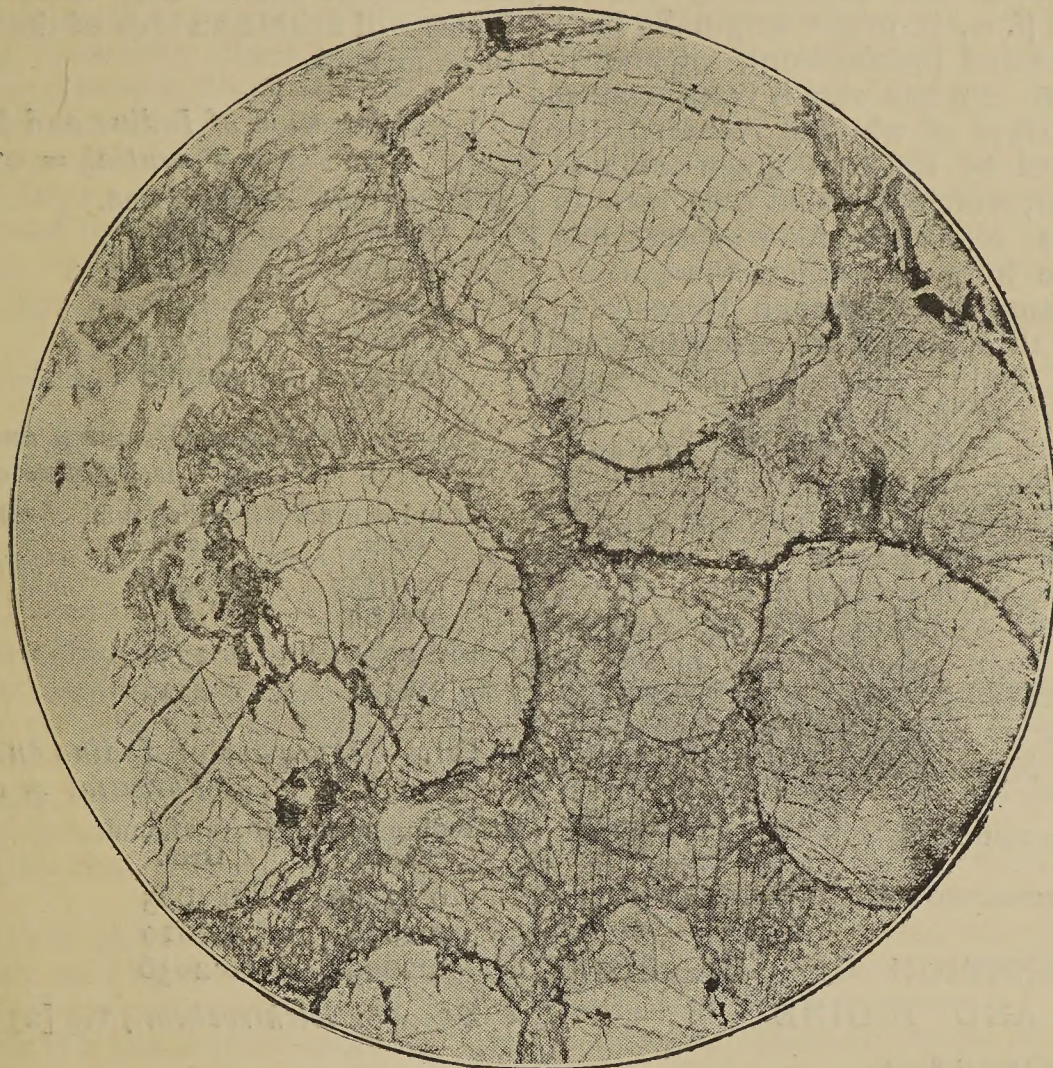


FIG. 1.—Section of the Diamond-bearing Eclogite. Pyropes with narrow kelyphite borders, and chrome diopside intercrystallised. The clinopinacoidal cleavage of latter visible in the lower part of the section.

(b) *Chrome-diopside*. — The mineral described under that name by Professor Lewis, and referred to by others as omphacite or sahlite. The individuals are sometimes about a quarter of an inch long. In thin slices it is a pale dullish green colour, inclining to olive; under the microscope, a pale sea-green, with a trace of pleochroism. It has one strongly marked cleavage, not, however, nearly so close as in ordinary diallage, and a second weaker,

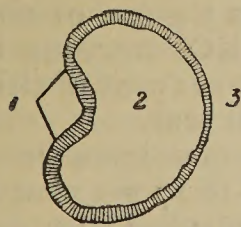


FIG. 2.—Garnet and Diamond (diagrammatic, nearly twice natural size). (1) Diamond, (2) garnet, (3) kelyphite rim.

sometimes approximately at right angles to it.* On examining flakes, obtained by crushing, I find the strong cleavage to be clinopinacoidal and the other probably basal, and obtain on a clinopinacoid an extinction of 35° with a prism edge. It is, in fact, identical with the pyroxene described by Professor Lewis† as chrome-diopside. In it (though rarely) small rounded enclosures of a greenish mineral aggregate much blackened with opacite. I regard them as alteration products of a ferri-ferous olivine. This diopside, at the exterior and along

indicated. Now and then a tiny film of brown mica occurs in this part or even in a crack in the diopside.

It is this alteration product which gives the mottled aspect mentioned above as visible to the unaided eye, so this is not indicative of a third important constituent in the original rock. In one of the slices the mica just named attains a larger size (about 0.03 inch across), has a fairly idiomorphic (hexagonal prism) outline, and is not restricted to the margin of the garnet. In this case it is generally associated with calcite,* which it tends to surround, and that in one place encloses a radiating acicular mineral (? a zeolite), in another the calcite, or some other carbonate, is mixed with a serpentinous material. Distinct granules of iron oxide are practically absent from the slices, though here and there it may be indicated by some opacite. I have not found spinel, or rutile, or zircon, or pseudobrookite. In fact, putting aside the diamonds, the rock in its unaltered condition was a coarsely holocrystalline mixture of chrome-diopside and garnet, with a few small enclosures of olivine,—in other words, it was a variety of eclogite and of igneous origin.†

2. A fragment (probably about one quarter) of a flattish ovoid boulder.—The two broken surfaces, which are

* From the facts I think it probably of secondary origin. It reminds me sometimes of the brown mica produced by contact metamorphism.

† I am, of course, aware that eclogite, in the past, has been regarded by some geologists as a metamorphic rock. Apart from the fact that several rocks once assigned to this class are now, with good reason, regarded as igneous, I have had several opportunities of studying eclogite, and have no doubt as to its origin. Take away the alkali from a magma with the chemical composition of a diorite, and the result would be garnets in place of felspar, *i.e.*, an eclogite.

* One may give a general idea of their relative importance by comparing them to the columns and cross-joints in some basalts.

† *Loc. cit.*, p. 21.

nearly at right angles, measure 5 and $5\frac{1}{2}$ inches, roughly, and it is about $3\frac{1}{4}$ inches high. The rock very closely resembles the one just described, except that mica occurs rather oftener and in larger flakes; perhaps the garnets (here also not quite regularly distributed) are slightly more numerous. The outer surface is not quite so well preserved, though enough remains to show that it also has been smooth, and a few thin veins of a white mineral (calcite?) traverse the rock. On this surface, near the meeting of the two fractures, and exposed by the removal of a little material (*i. e.*, it might originally have been just hidden) is a diamond (octahedron), apparently about 0.1 inch in diameter. On one side it rests against a pyrope, the adjacent surface of which is incurved, the two minerals being parted by the dull green-coloured kelyphite rim of the latter, which is about 0.03 inch in thickness. Thin sections of this boulder correspond almost exactly with those from the other, the garnets showing precisely the same tints, though traces of a cleavage (roughly parallel throughout) are perceptible on close inspection, and are distinct under the microscope. In garnet such a structure commonly indicates pressure, and the general parallelism accords with this explanation, but the other constituents show no signs of crushing. The "kelyphite" rims to the garnets are perhaps slightly broader, and the brown mica passes into a green (chloritic?) mineral, and occupies cracks in the garnet a little more frequently, but, as before, the constituents tend to lie parallel rather than radially. One or two of the diopsides show fine oscillatory twinning. The cracks are occupied with calcite or some altered carbonate. There is no real difference between this eclogite and the last-named one.

(To be continued.)

ELECTROLYTIC SEPARATION OF CHLORINE, BROMINE, AND IODINE.

By H. SPEKETER.

THE electromotive forces necessary for the electrolytic decomposition of the halogen acids are the following:— $\text{HCl} = 1.31$ volt, $\text{HBr} = 0.94$ volt, $\text{HI} = 0.52$ volt. Attempts made to separate the halogens by successively increasing the electromotive force from its lowest to its highest power have not been attended with satisfactory results.

Iodine, for example, has not been completely separated from the other halogens, even when increasing the electromotive force to 1.2 volts and removing the iodine formed by means of sulphide of carbon. This want of success appears to be due to the diffusion of the free iodine towards the cathode, where it is re-converted into hydriodic acid. We can, however, effect a quantitative separation by using a platinum cathode and an anode of perfectly pure silver. Under these conditions, the electromotive force of the decomposition can be calculated by Nernst's formula. The electrolysis is carried out in normal sulphuric solution. The iodine is precipitated in the form of iodide of silver on the anode when the strength of the current is below 0.13 volt, and the bromine when it is below 0.35 volt. As for the chlorine it is preferable to determine it in the ordinary manner by Volhard's method.

To effect the electrolysis, a thermopile of constant electromotive force is preferable, and a resistance-bar should be placed in the circuit so that the current may be regulated at will.

The vessel in which the electrolysis is carried out is a narrow test-tube fitted with a platinum cathode and an anode of pure silver foil.

During the whole time of the operation a current of hydrogen should be passed through the liquid for the purpose of clearing away any air or oxygen from the cathode. If this precaution be not taken, bromide and chloride of silver will be precipitated on the anode at the same time

as the iodide. In fact, in a solution of the halogen acids, the silver gives off hydrogen at the cathode, and if this hydrogen is continually eliminated by oxygen and air the haloid salts of silver will be deposited at the anode even without the use of any current at all.

A sensitive galvanometer in the circuit will show the exact moment when each halogen is completely eliminated from the solution.

The precipitate on the anode must be carefully washed and dried at 120° . The results given in the following tables will enable an idea of the exactitude of this method to be formed.

I.—Separation of Iodine and Chlorine. Difference of Potential = 0.13 volt.

Iodine used. Grm.	Iodine found. Grm.	Iodine used. Grm.	Iodine found. Grm.
0.29087	0.2892	0.1588	0.1598
0.0481	0.0480	0.2290	0.2565
0.3807	0.3773	0.15437	0.1532
0.2394	0.2386		

II.—Separation of Bromine and Chlorine. Difference of Potential = 0.35 volt.

Bromine used. Grm.	Bromine found. Grm.	Bromine used. Grm.	Bromine found. Grm.
0.19437	0.1940	0.19625	0.1958
0.1062	0.1041	0.19047	0.1883
0.27354	0.2736	0.18994	0.1906
0.2122	0.2111	0.18651	0.1836

III.—Separation of Iodine and Bromine. Difference of Potential = 0.13 volt.

Iodine used. Grm.	Iodine found. Grm.	Iodine used. Grm.	Iodine found. Grm.
0.17066	0.1685	0.1078	0.1080
0.1636	0.1610	0.1235	0.1218
0.2029	0.2036	0.1356	0.1348

—Zeit. für Elektrochem., v., [23], p. 539.

THE ESTIMATION OF TARTARIC ACID IN THE PRESENCE OF CITRIC ACID.

By A. BORNTRÖGER.

THE author shows that a solution containing 10 grms. of KCl and 2.5 grms. of neutral anhydrous citrate of potash in 100 c.c. of water, completely dissolves 1 gm. of bitartrate of potash at the ordinary temperature, while the solubility of the bitartrate is much less if the neutral citrate is replaced by 2.5 grms. of citric acid. If the 10 per cent solution of KCl contains both 2.5 per cent of neutral citrate and 2.5 per cent of citric acid the solubility of the bitartrate is still less.

In the analysis of lemon-juice we take 20 grms. of the sample (containing 16 to 17 per cent of the mixed acids), dissolve in water, neutralise with caustic potash, add 5 grms. of KCl, and dilute to 50 c.c. We then add 5 grms. of a 50 per cent solution of citric acid, and shake until the precipitate of bitartrate of potassium commences to appear; the whole is then allowed to stand for a night; filter off the bitartrate, wash first with a 10 per cent solution of KCl which has only just been saturated with bitartrate of potash, then with a solution of pure KCl. The precipitate is then dissolved and titrated.

The author has studied the effects of variable proportions of the two acids, and has arrived at the following conclusions:—

1. By using 5 grms. of citric acid as precipitant satisfactory results were obtained (97.3 per cent to 101.3 per cent) when the neutralised solution contained 1 gm. of bitartrate + 0.5–4 grms. of citric acid, 3 grms. of bitartrate + 3–4 grms. of citric acid, or 4 grms. of bitartrate + 3–5 grms. of citric acid.

2. By using 3 grms. of citric acid as precipitant satisfactory results are obtained (97.3 to 101.4 per cent) when the neutralised solution contained 1 gm. of bitartrate + 0.5—1 gm. of citric acid, 2 grms. of bitartrate + 0.5—2 grms. of citric acid, or 3—4 grms. of bitartrate + 1—2 grms. of citric acid.

With a larger proportion of bitartrate with regard to the citrate, the results are too high on account of the precipitation of a difficultly soluble acid citrate. When we have to deal with a solution containing both tartaric and citric acids, it is necessary to take such a quantity of citric acid corresponding to 3 grms. of acidity (citric), then add 5 grms. of KCl, neutralise with potash, dilute to 50 c.c., and precipitate as already described with 3 to 5 grms. of citric acid. If the proportions of the two acids do not come within the above limits, a fresh estimation must be made, and the proportions regulated by adding, according to the case, citric acid or a known weight of tartaric acid.—*Zeit. Anal. Chem.*, xxxvii., [8], 477.

ON A NEW METHOD FOR THE ESTIMATION OF FORMIC ALDEHYDE.

By O. BLANK and H. FINKENBEINER.

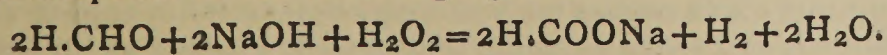
THE old method of estimating formic aldehyde which consisted of titrating the solution with ammonia, and which was in general use, gave results varying considerably from those given by methods now practised. These give very concordant results, and for solutions containing from 20 to 40 per cent of formic aldehyde, figures which are about 1.5 per cent higher than those given by the ammonia method.

The new method, which is based on the oxidation of formic aldehyde into formic acid by peroxide of hydrogen in alkaline solution, and the titration of the excess of alkali, is quite as exact as the commercial methods just mentioned. The estimation is conducted as follows: 3 grms. of the solution of formic aldehyde under examination (or 1 gm. in the case of solid formic aldehyde) are weighed out carefully and placed in a tall conical flask containing 25 c.c. of double normal soda (30 c.c. when the concentration of the formic aldehyde is greater than 45 per cent). The mixture is then immediately treated with 50 c.c. of peroxide of hydrogen at from 2.5 to 3 per cent; in the case of the peroxide of hydrogen having an acid reaction, the acidity should be determined and deducted from the final result. The peroxide of hydrogen must be added gradually (taking about three minutes) by means of a funnel; after two or three minutes the funnel is rinsed with water, and the excess of alkali is titrated with a double normal solution of sulphuric acid; in very exact analyses the water used for rinsing should be boiled first to drive off any carbonic acid. Litmus is used as an indicator (Portes Ruyssen, *Zeit. f. Anal. Chem.*, xvi., p. 25; *Gazz. Chim. Ital.*, xx., p. 394).

If we have to deal with solutions containing less than 30 per cent of formic aldehyde the mixture should be allowed to stand for about ten minutes after the addition of the peroxide of hydrogen, for the reaction to be complete.

The centesimal contents of formic aldehyde is obtained directly by multiplying the number of c.c. of soda employed in the titration by 2 if 3 grms. of the solution was originally taken, or by 6 if we took 1 gm. of the solid formic aldehyde.

The reaction takes place with the disengagement of a considerable amount of heat and production of froth. It corresponds to the following equation—



We are not able to say whether the reaction takes place quantitatively in the manner indicated, or whether there

is a further oxidation of the formic acid into carbonic acid, $\text{H.CHO} + \text{NaOH} + \text{H}_2\text{O}_2 = \text{H.COONa} + 2\text{H}_2\text{O}$.

We did not consider it necessary to estimate the hydrogen set at liberty, as a part of it would no doubt combine with the excess of peroxide of hydrogen. The presence of hydrogen was, however, proved by the inflammability of the gas given off, and by the explosion of a mixture of this gas with air. After removing the excess of peroxide of hydrogen, the formic acid can be easily estimated by nitrate of potash in the usual manner.*

A mixture of 0.5 gm. of formic aldehyde, 5 c.c. of double normal soda, and 10 c.c. of peroxide of hydrogen was titrated after standing for half-an-hour, and then being gently heated on a water-bath with 10 grms. of nitrite of potash for half-an-hour. After adding 5 grms. of bichloride of mercury the mixture was digested for two hours in a flask fitted with a reflux condenser.

The following results were obtained:—

- (a) 3.1267 grms. HgCl representing 39.8 per cent CH_2O
(b) 3.4941 " " " " 44.5 " " "

After oxidation by means of peroxide of hydrogen we found in the same manner (a) 39.7 per cent CH_2O , and (b) 44.5 per cent CH_2O .

Other methods in common use gave (a) 39.8 per cent CH_2O , (b) 44.5 per cent CH_2O .

We have used our method for the estimation of several other aldehydes—acetic aldehyde, paraldehyde, benzoic aldehyde, &c.

Acetic aldehyde reacts much more slowly than formic aldehyde with peroxide of hydrogen and caustic soda; but after half-an-hour an abundant disengagement of hydrogen takes place. We have still to decide whether this reaction is quantitative.

To be complete this reaction requires several hours. In the case of paraldehyde the action of the peroxide of hydrogen is even slower, but after the addition of a trace of ferric salt, the disengagement of gas was extremely slight though quite regular.

Benzoic aldehyde reacts a little more energetically, especially in the presence of a trace of ferric salt, but to be complete a considerable time is necessary. Even the addition of methylic alcohol—which is not attacked by peroxide of hydrogen under these conditions—to help the solution of the aldehyde did not notably accelerate the reaction.—*Berichte der D. Chem. Gesel.*, 1898, p. 2979.

ESTIMATION OF FAT IN ALIMENTARY PRODUCTS, MEAT, &c.

By L. LIEBERMANN and S. SZEKELY.

BOIL 5 grms. of the substance for thirty minutes with 30 c.c. of a 50 per cent ($d=1.541$) solution of caustic potash in a specially made flask, of which the following is the description:—The body of the flask must be 7.5 c.m. in diameter and 5.5 c.m. high, with a flat bottom; the neck must be 19.5 c.m. in length, and 3.5 c.m. in diameter throughout. When filled half way up the neck it should contain 290 c.c. A gauge mark must be made at 240 c.c.

After boiling, the contents of the flask are allowed to cool; 30 c.c. of alcohol at 90—94 per cent are then added, and the whole again heated for ten minutes. After cooling again 100 c.c. of sulphuric acid at 20 per cent ($d=1.145$) are carefully added, while constantly stirring, the whole being kept cool to prevent the loss of volatile fatty acids. The solution, which will finally contain an excess of about 4.4 grms. of sulphuric acid, is now mixed with 50 c.c. of petroleum ether ($d=0.6$ to 0.7 ; and boiling point

* A blank experiment with nitrite of potash and bichloride of mercury showed that these two substances do not react under these conditions. It is only after the lapse of a very long time that a faint cloudiness can be noticed.

=60°); the flask must now be well corked and shaken up about 30 times at intervals of one or two minutes. A saturated solution of chloride of sodium is then added so as to fill the flask up to the middle of the neck, and make the level of the aqueous solution below the ether, near the 240 c.c. mark. Shake again several times, and place the flask in warm water.

As soon as the layer of ether (containing most of the fats) separates out, 20 c.c. are taken by means of a pipette, and transferred to a 150 c.c. flask with a wide neck. Add 40 c.c. of neutral alcohol at 96 per cent, and titrate with decinormal alcoholic potash. The solution is then again transferred to a tared covered glass crucible about 80 c.c. in diameter. Evaporate slowly to dryness on a water-bath, heat in an oven at 100° for an hour, and weigh. To calculate the amount of fat, it is necessary to deduct the amount of potash contained in the soap, and add the corresponding weight to the glyceric radical. As 1 c.c. of decinormal potash corresponds to 0.00391 grm. of potassium, and to 0.00136 grm. of C_3H_5 , as many times 0.00255 grm. must be deducted as c.c. of potash have been used in the titration.

The amount of fat may then be calculated according to the formula—

$$F = \left[\frac{S - 0.01 - (k \times 0.00255)}{a} \right] \times 250.$$

in which F represents the percentage of fat present in the substance; S the weight of potash soap extracted from 20 c.c. of petroleum ether; k the number of c.c. of decinormal potash; and a the weight of the substance analysed.—*Arch. Physiol.*, lxii., 360.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 15th, 1899.

Professor T. E. THORPE, F.R.S., President, in the Chair.

MESSRS. A. R. Foulerton, S. B. Schryver, and J. P. de Castro were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Percy Kay, 3, Phene Street, Chelsea, S.W.; Hugh Main, 45, The Vicarage, Old Charlton, Kent.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—

Robert Henry Aders, George Dekeyne Atkinson, Percy Bean, Walter Lionel Blackman, Wilfred Carpmael, James Connah, B.Sc., Henry Meldola Danziger, Frederick Doyle, Frederick Charles Dunscombe, William Frederick Eichenauer, F. N. Ashcroft Fleischmann, William Gordon Fraser, Frederick Hutton Getman, Julius Hübner, Edward Charles Johnson, Arthur Alexander Leon, James McAlley, Robert McClumpha, George Alfred Parkes, Stanley John Peachey, Eskricke Sidney Phillips, B.A., Sidney Rossiter, Henry Royal-Dawson, William F. John Shephard, John William Shephard, B.Sc., Charles Simmonds, B.Sc., John Ward Stainer, Samuel Stansfield, B.Sc., George Hardstaff West, B.Sc., Christopher Joseph Whittaker.

Of the following papers those marked * were read:—

*84. "On the Decomposition of Chlorates, with special reference to the Evolution of Chlorine and Oxygen." By W. H. SODEAU, B.Sc.

Some chlorates, on being heated, give off almost all their chlorine as such, whilst other chlorates give none. According to Schulze, the chlorate breaks up into chloride and oxygen, the chlorine evolved being due to the nascent oxygen attacking the chloride, whilst Spring and Prost regard the chlorate as decomposing into oxide, chlorine, and oxygen, the chlorine being more or less re-absorbed.

The author points out that in addition to these two theories two others are possible: (1) that chlorates may break up in both of these ways simultaneously, and (2) that chloride and oxide may represent the balanced action of chlorine and oxygen.

His experiments have been made chiefly with potassium and barium chlorates. The former gives no chlorine, whether the pressure of the evolved gas be kept at 1 m.m. or at 1 atmosphere. With barium chlorate, however, 0.066 per cent of the total chlorine was evolved when the pressure was kept at 1 to 2 m.m., and the duration of the experiment 233 minutes, whilst at atmospheric pressure, 0.093 was obtained when the duration was 165 minutes, but when very rapidly decomposed (half a minute), the percentage of chlorine evolved rose to 0.705. These are the averages of several experiments.

From the results of his experiments, the author concluded that when barium chlorate is heated, it undergoes two decompositions at the same time: (a) an exothermic decomposition into chloride and oxygen, (b) an endothermic decomposition into oxide, chlorine, and oxygen, and that no appreciable reaction takes place between the chloride and oxygen (or chlorate), or between the oxide and chlorine, but that the increase of chlorine in a rapid decomposition may be ascribed to the great rise of temperature favouring the endothermic reaction. He believed that potassium chlorate decomposed directly into chloride and oxygen. Further experiments were being conducted on the behaviour of manganese oxides with potassium chlorate, and on the decomposition of pure lead and calcium chlorates. The experiments already performed with these chlorates appear to confirm the author's view that these two independent reactions occurred.

*85. "Action of Hydrogen Peroxide on Formaldehyde." By A. HARDEN, M.Sc., Ph.D.

When solutions of hydrogen peroxide and formaldehyde are mixed, no reaction appears to take place, but when the liquid is made strongly alkaline with soda, hydrogen is evolved. The reaction occurs according to the equation $H_2O_2 + 2CH_2O + 2NaOH = 2H \cdot CO_2Na + H_2 + 2H_2O$. Hydrogen peroxide, therefore, when treated with alkaline formaldehyde, gives a volume of hydrogen exactly equal to the volume of oxygen which it would give with potassium permanganate and sulphuric acid.

The reaction proceeds slowly and incompletely unless a large excess of alkali be present. When hydrogen peroxide is treated with excess of formaldehyde, the reaction takes place rapidly and completely, and the hydrogen which is evolved is pure. When, on the other hand, formaldehyde is treated with excess of hydrogen peroxide, the reaction is incomplete and proceeds very slowly, whilst the gas evolved contains oxygen. Hence the reaction does not appear adapted for the quantitative estimation of formaldehyde in aqueous solutions.

Cuprous oxide and soda give a somewhat similar reaction with formaldehyde. This reaction was described by Loew (*Ber.*, 1887, xx., 145) as a catalytic reaction, but it appears in reality to be a quantitative one, expressed by the equation—

$Cu_2O + 2NaOH + 2CH_2O = Cu_2 + H_2 + 2H \cdot CO_2Na + H_2O$. Cupric oxide also gives a similar reaction, two atoms of hydrogen being liberated for each atom of oxygen in the oxide.

When caustic soda and then formaldehyde are added to a solution of copper sulphate and the liquid gently warmed, the cupric hydroxide is reduced to cuprous oxide without evolution of hydrogen, and when the temperature is subsequently raised, the cuprous oxide reacts as described above. When, on the other hand, caustic soda is added to a boiling solution of copper sulphate, the liquid cooled, and formaldehyde then added, no reduction to cuprous oxide occurs on warming, but metallic copper is formed, and twice as much hydrogen is evolved as in the previous case.

Manganese dioxide does not appear to be reduced by

formaldehyde, whilst the oxides of mercury and bismuth are reduced without evolution of hydrogen.

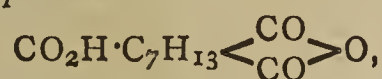
DISCUSSION.

Mr. CROSS said that he regarded the author's results as additional evidence that hydrogen peroxide tends to react as H_2O_2 , as it was clear that, in this case, it could not react as H_2O, O .

Dr. DEBUS pointed out that, in acting as an oxidising agent, hydrogen peroxide usually broke up into water and oxygen, but since aldehydes in many reactions behave as hydrides, we might suppose that the equation $2H \cdot CHO + (HO)_2 = 2(HO \cdot CHO) + H_2$ represented the change, the hydrogen set free coming from the aldehyde.

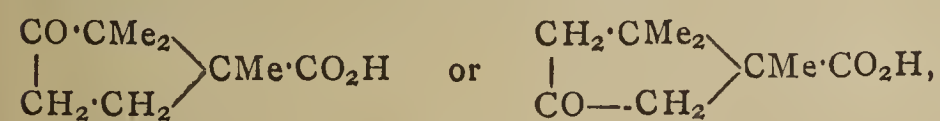
*86. "Homocamphoronic and Camphoronic Acids." By ARTHUR LAPWORTH and EDGAR M. CHAPMAN.

α -Dibromocamphor, though scarcely affected by the ordinary mild oxidising agents, is rapidly attacked by dilute nitric acid in presence of silver nitrate. The greater portion of the substance is reduced to monobromocamphor and camphor, but a small quantity is converted into a neutral *nitro*-compound, $C_{10}H_{14}N_2O_6$, which crystallises in beautiful, orthorhombic prisms melting at $93-94^\circ$. A still smaller quantity of the dibromo-compound is converted into an *acid*, $C_{10}H_{16}O_6$, which is found to be identical with the substance obtained by Forster (*Trans.*, 1896, lix., 49) on oxidising bromocamphorenic acid with dilute permanganate. The authors find that this acid is tribasic, and for it they propose the name *homocamphoronic acid*; it is an open chain tricarboxylic acid, and its constitution must be represented by one of two formulæ, $CO_2H \cdot CMe_2 \cdot CMe(CO_2H) \cdot CH_2 \cdot CH_2 \cdot CO_2H$ or $CO_2H \cdot CH_2 \cdot CMe_2 \cdot CMe(CO_2H) \cdot CH_2 \cdot CO_2H$, of which the former seems to be the more probable. Homocamphoronic acid is optically active; in 2 per cent aqueous solutions $[a]_D = -34.96^\circ$. It is somewhat sparingly soluble in water, and separates from aqueous solution in small prisms which give off water and melt, according to the rate of heating, between 180° and 208° , the latter temperature being probably the true melting point. *Anhydrohomocamphoronic acid*—



is made by heating the acid or by warming it with acetyl chloride; it crystallises in prisms melting at $86-87^\circ$. The aniline derivative, $(CO_2H)_2 \cdot C_7H_{13}CO \cdot NHPh$, melts at $98-100^\circ$, and the paratoluidine derivative, $(CO_2H)_2 \cdot C_7H_{13} \cdot CO \cdot NH \cdot C_7H_7$, at $163-164^\circ$.

When anhydrohomocamphoronic acid is heated to $200-260^\circ$ it loses carbon dioxide and yields an acid having the formula $C_9H_{14}O_3$. This substance is a saturated cyclic ketonic acid having the structure—



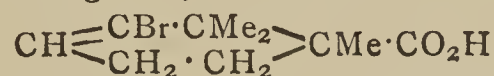
and, therefore, containing the carbon atoms in the position assumed by Bredt and Perkin for nine of the ten atoms in camphoric acid. The substance is, in fact, identical with a ketonic acid obtained by J. Walker as a by-product in the electrolysis of ethyl allocamphorate. Dr. Walker was good enough to send the authors a small specimen of his acid for comparison, and the identity of the two substances has been completely established; he has, moreover, agreed to the name *camphoronic acid*, which the authors propose for it. It melts at 228° , and has all the properties assigned to it by Walker. The phenylhydrazone, $CO_2H \cdot C_8H_{13} : N \cdot NHPh$, crystallises in colourless needles melting at 174° . The *bromophenylhydrazone*, $C_{15}H_{19}O_2N_2Br$, forms transparent prisms and melts at $194-195^\circ$. The *semicarbazone* crystallises in needles and melts and decomposes at $230-232^\circ$.

When camphoronic acid is very carefully oxidised with dilute nitric acid, a large quantity of camphoronic acid, which is apparently the sole product, is obtained.

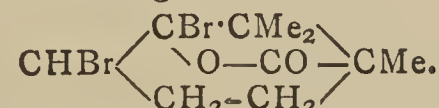
*87. "Action of Silver Compounds on α -Dibromocamphor." By ARTHUR LAPWORTH.

The formation of homocamphoronic acid from α -dibromocamphor by the action of dilute nitric acid and silver nitrate is preceded by the production of an unsaturated acid, $C_{10}H_{15}BrO_2$, identical with bromocamphorenic acid, which was first obtained by the reduction of α -dibromocampholid (Forster, *Trans.*, 1896, lix., 46). This substance may be obtained by heating a solution of α -dibromocamphor in acetic acid or alcohol with silver nitrate, acetate, or oxide; the amount formed is small, however (10—20 per cent), the greater portion of the dibromocamphor undergoing reduction.

The formation of bromocamphorenic acid appears at first to be due to hydrolysis, represented empirically by the equation $C_{10}H_{14}Br_2O + H_2O = C_{10}H_{15}Br_2 + HBr$. As bromocamphorenic acid at once loses hydrogen bromide when treated with cold dilute potassium permanganate, and is subsequently converted into homocamphoronic acid, it seems certain that it contains the group $-CH=CH-$ as a part of the closed chain; and as dibromocamphor contains the group $-CBr_2 \cdot CO-$, it would appear that, in the formation of bromocamphorenic acid, these two carbon atoms are separated, and that one of them enters the second pentamethylene ring. Of the possible formulæ for bromocamphorenic acid, which are, of course, easily derived from the two possible formulæ for homocamphoronic acid (see preceding note) the formula—



is the one which is most in accordance with the facts which have been observed, the corresponding formula for dibromocampholid being—



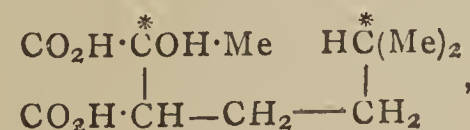
88. "The Colouring Matter of Cotton Flowers." By A. G. PERKIN.

The flowers of the cotton plant, *Gossypium herbaceum*, are employed as a dye-stuff in the Manipur district of India. They contain as glucoside a new colouring matter, *gossypetin*, $C_{16}H_{12}O_8$, soluble in alkalis with an orange-red colour, becoming green on oxidation. The *hexacetyl* compound, $C_{16}H_6O_8Ac_6$, colourless needles, m. p. $212-216^\circ$; the *sulphate*, $C_{16}H_{12}O_8 \cdot H_2SO_4$, the *hydriodide*, $C_{16}H_{12}O_8 \cdot HI$, orange-red needles, and the *monopotassium* salt, $C_{16}H_{11}O_8K$, a crystalline powder, have been prepared. *Gossypetin* contains no methoxyl groups, and on fusion with alkali yields phloroglucinol and protocatechuic acid. It is probably a member of the flavone group of colouring matters. *Gossypetin* is similar to, but not identical with, *thujetin*, which is present in *Thuja occidentalis* (Kawaler, *Fahresbericht*, 1858, 512).

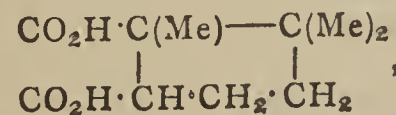
Note on Rottlerine.—The decomposition products of rottlerine, $C_{33}H_{30}O_9$, a colouring matter of kamala, *Mallotus Phillipinensis*, previously described (*Trans.*, 1893, lxx., 981; 1895, lvii., 230), are with fused alkali, acetic and benzoic acids, and with nitric acid *o*- and *p*-nitrocinnamic acids. It has now been found that fused alkali at $220-240^\circ$ yields also phloroglucinol.

89. "Experiments on the Synthesis of Camphoric Acid." By H. A. AUDEN, W. H. PERKIN, jun., and J. L. ROSE.

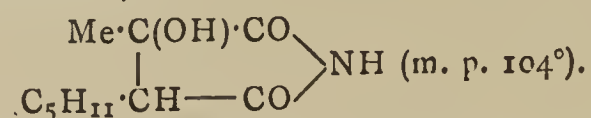
These experiments were instituted with the object of preparing an acid of the formula—



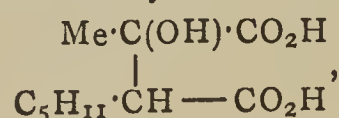
in the hope that it might prove possible to eliminate water between the points marked *, and thus obtain an acid,—



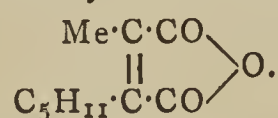
which would have the constitution first suggested by Perkin (*Proc.*, 1896, xii., 191) as a possible expression of the constitution of camphoric acid. Ethyl isoamylacetate was dissolved in ether and treated at a low temperature with potassium cyanide and hydrochloric acid, when ethyl α -isoamyl- $\beta\beta$ -hydroxycyanobutyrate, $\text{Me}(\text{CN})\text{C}(\text{OH})\cdot\text{CH}(\text{C}_5\text{H}_{11})\cdot\text{CO}_2\text{Et}$, was obtained as a thick oil, which on hydrolysis with alcohol and hydrochloric acid, yielded as principal product methylhydroxyisoamylsuccinimide,—



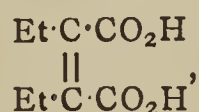
This substance, when boiled with sodium carbonate, is first converted into the corresponding amide, which crystallises from water and melts at 183° , and then into $\alpha\alpha$ -methylhydroxy- α' -isoamylsuccinic acid,—



which melts at 66° , and yields a silver salt of the formula $\text{C}_{10}\text{H}_{16}\text{O}_5\text{Ag}_2$. As this acid has the constitution represented by the formula given at the commencement of this abstract, experiments were next made with the object of eliminating water in such a way as to obtain a saturated acid of the same composition as camphoric acid, but without success. When the acid is subjected to distillation, water is eliminated and an oil, distilling at 260° , is obtained, which after careful investigation has been found to be methylisoamylmaleic anhydride,—

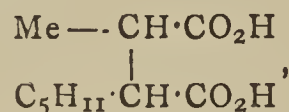


This anhydride dissolves in potash solution, but on acidifying, the anhydride, and not the acid, separates, a behaviour which is exactly similar to the case of xeronic acid,—



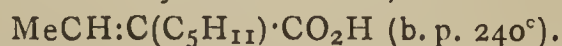
which, when set free from its salts, is obtained in the form of its anhydride.

The solution of methylisoamylmaleic anhydride in benzene gives, with aniline, the anil $\text{C}_{16}\text{H}_{19}\text{O}_2\text{N}$, which crystallises from methyl alcohol and melts at 70° . When the anhydride is reduced with hydriodic acid and phosphorus, it yields a mixture of *cis*- and *trans*-methylisoamylsuccinic acids,—

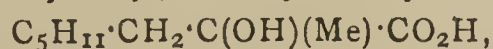


the former of which melts at 92° and the latter at 142° (see following abstract).

Ethyl-isoamylacetate is readily reduced by sodium amalgam, forming α -isoamyl- β -hydroxybutyric acid, $\text{Me}\cdot\text{CHOH}\cdot\text{CH}(\text{C}_5\text{H}_{11})\cdot\text{CO}_2\text{Et}$, a thick oil, which, on distillation, decomposes with elimination of water and formation of α -isoamylcrotonic acid,—



That ring-formation had not taken place in this case was shown by the fact that the acid obtained is unsaturated, and, on oxidation, yields isobutylic acid, $\text{C}_5\text{H}_{11}\text{CO}_2\text{H}$. When isoamylacetone, $\text{C}_5\text{H}_{11}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{Me}$, is treated with hydrocyanic acid and the product hydrolysed, a small quantity of α -hydroxy- β -isoamylisobutyric acid,—



is formed, which melts at 65° , and is isomeric with the isoamylhydroxybutyric acid mentioned above.

90. "Methylisoamylsuccinic Acid." I. By W. TREVOR LAWRENCE.

The author is preparing methylisoamylsuccinic acid in

large quantities, in order to obtain from it, if possible, by oxidation or bromination, and subsequent splitting off of water or hydrogen bromide respectively, an acid possessing the constitution of camphoric acid (see preceding abstract) suggested by Perkin in 1896, and independently in 1897 by Bouveault (*Bull. Soc. Chim.*, 3, xvii., 990); this paper contains only such results as confirm those of Auden, Perkin, and Rose.

When ethyl α -methyl- α' -cyansuccinate, isoamylbromide, and sodium ethylate are heated, in molecular proportions, and the product of the condensation distilled under diminished pressure, ethyl α -methyl- α' -cyan- α' -isoamylsuccinate, $\text{CO}_2\text{Et}\cdot\text{C}(\text{C}_5\text{H}_{11})(\text{CN})\cdot\text{CH}(\text{Me})\text{CO}_2\text{Et}$, is obtained (b. p. 182° , 30 m.m.), which, on hydrolysis with alcoholic potash, gives, after acidifying, a semi-solid acid mass, probably consisting of the cyansuccinic acid. A similar acid was also prepared as follows:—

Isoamylacetic acid is converted by bromine and phosphorus pentabromide into the acid bromide of α -bromisoamylacetic acid, which, with alcohol, gives ethyl α -bromisoamylacetate, $\text{C}_5\text{H}_{11}\text{CHBr}(\text{CO}_2\text{Et})$, (b. p. 146° , 65 m.m.); this condenses with ethyl sodio cyanacetate to form ethyl α -cyan- α' -isoamylsuccinate (b. p. 196° , 35 m.m.).

Ethyl α -cyan- α' -isoamylsuccinate,—



is converted into isoamylsuccinic acid,—



(m.p. 76°), on hydrolysis, and is identical with the acid obtained by Fittig and Schirmacher (*Annalen*, 1898, ccciv., 295); on treatment with methyl iodide and sodium ethylate, it is converted into ethyl α -cyan- α' -methyl- α' -isoamylsuccinate, $\text{CO}_2\text{Et}\cdot\text{C}(\text{CN})(\text{Me})\cdot\text{CH}(\text{C}_5\text{H}_{11})\text{CO}_2\text{Et}$, (b. p. 185° , 30 m.m.), which, on hydrolysis, gives a similar cyansuccinic acid to the one mentioned above.

Both of these cyan-acids give, on hydrolysis, a mixture of *trans*- and *cis*-methylisoamylsuccinic acids,—

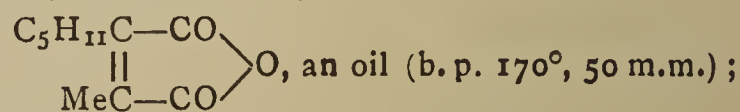


which may be separated either by distillation in a current of steam, in which the *cis*-acid is volatile, or by means of ligroin, in which the *trans*-acid is insoluble.

trans-Methylisoamylsuccinic acid crystallises from benzene or hot water in prisms (m. p. $141\text{--}142^\circ$), and is converted by acetyl chloride into the anhydride (b. p. 170° , 25 m.m.).

cis-Methylisoamylsuccinic acid is not easily re-crystallised; it is obtained from the pure anhydride as a crystalline powder (m. p. 93°); the anhydride is obtained as an oil (b. p. 187° , 50 m.m.) by the action of acetyl chloride. The anil melts at 116° .

This anhydride, heated with bromine and chloroform in a sealed tube for ten hours is converted into β -isoamylcitric anhydride,—



the free acid does not appear to exist.

On treatment with aniline, the anhydride, which reduces permanganate in the cold, is converted into the characteristic anil, which crystallises from methyl alcohol in needles, (m. p. 71°).

(To be continued).

Sulphate of Ammonia.—The prize of 500 guineas, offered by the Sulphate of Ammonia Committee for the best essay on "The Utility of Sulphate of Ammonia in Agriculture," has been awarded by the judges—Mr. J. Bowen-Jones, of Shrewsbury, and Dr. J. Augustus Voelcker, of London—to Mr. James Muir, M.R.A.C., formerly professor at the Royal Agricultural College, Cirencester; subsequently at the Yorkshire College, Leeds; now County Instructor in Agriculture to the Somerset County Council. Seventy-three essays were sent in.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

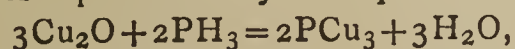
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 23, June 5, 1899.

Molecular Refraction, Molecular Dispersion, and Specific Rotatory Power of Compounds of Camphor with Aromatic Aldehydes.—A. Haller and P. Th. Muller.—The authors have determined the above indices for the compound benzylidene camphor and its analogues, with respect to the sodium line and the three rays of hydrogen, α , β , and γ , at a temperature $20^\circ \pm 0.2$ with Pulfrich's refractometer. The same constants were also calculated theoretically for the same rays. It was found that the addition of aldehydes to camphor has the effect not only of increasing the refraction and molecular dispersion, but also of considerably increasing the rotatory power of the molecules.

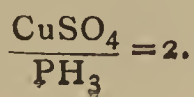
Use of Chlorate of Potash in Nitrate of Ammonium Explosives.—H. Le Chatelier.—Nitrate of ammonium explosives have come into general use in mines, but many accidents have occurred through admixtures of chlorate of potash. The author investigates the action of these two substances on one another, and finds that in reality an isomorphous mixture is formed of the two salts. The two salts are dissolved in a sufficient quantity of water to keep them in solution at the ordinary temperature. On cooling a small quantity of crystals is deposited, which can be examined.

Effect of Low Temperatures on certain kinds of Steel.—F. Osmond.—The author examines the properties of a series of nickel steels; finding that, if non-magnetic to start with, after immersion in liquid air for five minutes, magnetic properties are acquired. If the greater part of the nickel is replaced by manganese, the same is true. If these two metals are replaced by carbon (1.4 to 1.6 per cent of carbon by preference), and the steel, being heated to about 1050° , is plunged into iced water, two structural constituents are formed,—one hard, as normal steel, the other relatively soft, like manganese or nickel steels. After some moments' immersion in liquid air, the metal, on being brought back to ordinary temperature, is found to be profoundly modified. Its magnetic permeability and its permanent magnetism are increased; its density is decreased from 7.798 to 7.692. If one face was originally polished, the polish disappears. The explanation of these facts appears to be that the lowering of the point of allotropic transformation of iron is comparable with the lowering of the solidification-points of the solvents by the substances dissolved.

Action of Phosphoretted Hydrogen on Copper, Copper Suboxide, and Ammoniacal Salts of Copper.—E. Rubénovich.—In a previous paper the author described the result of his researches on the action of hydrogen phosphide on an aqueous solution of copper sulphate. The same method is now applied to the investigation of the action of this gas on other compounds of copper. On copper itself the gas appears to have the following action: $\text{PH}_3 + 3\text{Cu} = \text{PCu}_3 + 1.5\text{H}_2$. The copper phosphide formed slowly oxidises in an atmosphere of oxygen towards 100° with incandescence. On copper suboxide the reaction is represented by the equation—



the copper phosphide having the same properties as that formed as above. Hydrogen phosphide has no action on an ammoniacal solution of copper chloride. On the sulphate solution a phosphide, $\text{P}_2\text{Cu}_5\text{H}_2\text{O}$, is formed, the proportion of the constituents being—



With solutions of the formate and acetate of copper an oxidised compound, Cu_3PO , is formed, the proportion being

$$\frac{\text{Salt}}{\text{PH}_3} = 2.5, \text{ \&c.}$$

Aloïns.—E. Léger.—The author prepares and investigates the properties of two crystalline substances obtained from Natal aloes. Nataloïn, which has already been prepared, and another aloïn, differing from nataloïn in having one group less of CH_2 , and for this reason called homonataloïn. The following reactions enable these two aloïns to be distinguished from barlaloïn:—(1.) A solution of the substance, containing sulphuric acid, to which is added a grain of manganese dioxide or bichromate of potassium, turns a bright green colour. (2.) If a grain of ammonium persulphate is added to the sodium solution, a violet colour appears little by little.

Some Derivatives of Disymmetric Tetramethyldiamidodiphenylethane.—A. Trillat.—Already inserted.

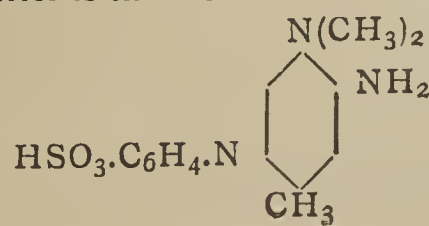
Some Colour Reactions of Oxycellulose.—Edm. Jandrier.—Oxycelluloses, particularly that obtained by the oxidation of cotton by means of potassium chlorate, by Leo Vignon's method, give, in a similar manner to all bodies of the aldehyde formation, colour reactions when treated with sulphuric acid in presence of a phenol.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxi., October 24, 1898.

Remarks on the Action of Acetylene on Nitrate of Mercury.—P. Köthner.—Basing his opinion on a series of analyses, the author has come to the conclusion that a product is formed by this reaction having the composition $\text{C}_2\text{Hg}_3\text{NO}_4\text{H}_2$, which he considers to be a nitrate of the carbide of mercury, $\text{HgC} \equiv \text{C.Hg} + \text{HgNO}_3 + \text{H}_2\text{O}$; K. H. Hofmann arrived at a different conclusion. He now proposes to try and find out the cause of this difference, which may possibly be due to a difference in the conditions under which the experiments are carried out. The ease with which the above compound gives off aldehyde has led to a synthetic method for the production of acetaldehyd by means of acetylene.

Naphthopicric Acid.—F. Kehrmann and W. Haberkant.—The authors have examined the raw product from the nitration of Martius yellow (dinitro- α -naphthol, $\text{OH.NO}_2\text{NO}_2$ -1:2:4; besides the trinitro- α -naphthol already known, they have obtained by fractional crystallisation an isomer fusible at 145° . This latter, by oxidation with dilute nitric acid, gives 1:2:4-nitrophthalic acid, in which the third nitro-group ought to be found in one of the β positions of the second nucleus. The authors have, by means of Diehl and Merz's naphthopicric acid, prepared diaminonaphthoquinone-imide; they found that this latter body, when heated in aqueous acid solution, is easily transformed into a mixture of diaminonaphthoquinone and aminonaphthoquinone, while the expected oxynaphthoquinone-imidic derivative was not found.

Contributions to the Rules of Substitution in the Formation of Azoic Colouring-matters.—J. Pinnow and A. Matcowich.—One of the authors recently announced that *m*-amido-dimethyl-*p*-toluidine gives, with sulphonic dinitrobenzene, an azoic colouring-matter, the constitution of which was not established. The authors are now able to state that the azoic group is in the para-position with regard to the amido group, and that consequently the group "dimethyl-amido" is not opposed specially to the azoic group. The constitution of this colouring-matter is therefore—



The Transformation of Nicotic Acid into β -Amidopyridine.—Th. Curtius and E. Mohr.—By heating the ether of nicotic acid with hydrate of hydrazine, we obtain nicotic hydrazide, $C_5H_4N.CO.NH.NH_2$, fusible at $158-159^\circ$, of which the chlorhydrate crystallises in white needles fusible at 227° : this hydrazide, when shaken up in aqueous solution with benzaldehyde, gives the hydrazide of benznicotinic acid. When we add to a solution of hydrochlorate of nicotic hydrazide, a cold solution of two molecules of nitrite of sodium, and keep stirring and cooling, nicotic azide is formed; the ethereal solution of this azide, when digested with absolute alcohol until no more nitrogen comes off, gives β -pyridylurethane: if this latter body is digested with fuming HCl until no more carbonic acid comes off, the already-known hydrochlorate of β -amidopyridine is formed, $C_5H_4NNH_2 + 2HCl$, melting at $173.5-174.5^\circ$.

On β -Diazopyridine and β -Diamidopyridine. — A. Mohr.—The author has dinitrated the hydrochlorate of β -amidopyridine, and joined it in alcoholic solution with resorcline, thus obtaining pyrodine-nitro-resorcline, $C_5H_4N.N=NC_6H_3(OH)_2$, a colouring-matter which dyes wool and silk a yellowish brown in an acid or alkaline bath. In the pure state it occurs in prisms fusible at 218° . He also describes β -dinitro-amidopyridine, obtained by reacting with 1 molecule of nitrite of sodium on 2 molecules of hydrochlorate of β -amidopyridine. The solutions of dinitropyridine appear to decompose, even in the cold, when an attempt is made to reduce them by $SnCl_2 + HCl$. The reduction of dinitro-sulphonic acid by zinc powder and acetic acid is much sharper; a solution of pyridylhydrazine is obtained, which, when shaken up with benzaldehyde, gives benzal- β -pyridylhydrazine in needles fusing at $163-164^\circ$.

On the Hydrazines and the Azoic Compounds of the Pyridine Series.—W. Marckwald.—The author has already observed that the amido-group, α or γ , in pyridine prevents the dinitration, inasmuch as the dinitric derivatives decompose immediately on being formed; β -amidopyridine alone is able to give dinitric compounds. The author has attempted to prepare the hydrazines, starting from the α and γ chloropyridines; it is well known that these derivatives are transformed by ammonia into amidopyridines. While ammonia acts above 200° , hydrazine transforms the compounds, even quantitatively, in the desired manner at 150° .

MISCELLANEOUS.

Society of Arts.—The Albert Medal for the present year has been awarded by the President and Council to Sir William Crookes, F.R.S., for his extensive and laborious researches in chemistry and in physics, researches which have, in many instances, developed into useful practical applications in the Arts and Manufactures. Sir William Crookes was among the first to employ the spectroscope as an instrument of chemical research, and by its aid, in 1861, he discovered the metal thallium, the earliest of the series of the "rare metals." To his researches was also due the discovery of the various earths now so extensively employed in obtaining a large increase of light from illuminants. In 1872, he began the long series of experiments on radiation, of which the radiometer was the first outcome. This work on molecular physics in high vacua led to methods of producing extremely high vacua, which made possible the construction of the incandescent lamp. They also enabled the remarkable properties of the cathode rays (which are affording such important results in connection with surgery) to be discovered and developed. He has rendered important services to industrial chemistry, and long ago established a position as an authority on the chemistry of dyeing and

calico printing. His work in connection with the chemistry of agriculture also requires to be noted. His services to pure science have been acknowledged by the award of a Royal Medal, and of the Davy Medal of the Royal Society; and it is the application of these researches to industrial uses which led the Council of the Society to submit his name to the President for the award of the Albert Medal.—*Journal of the Society of Arts*, June 30, 1899.

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THE CHEMICAL NEWS.

VOL. LXXX., No. 2068.

THE PARENT-ROCK OF THE DIAMOND IN SOUTH AFRICA.*

By Professor T. G. BONNEY, D.Sc., LL.D., V.P.R.S.

(Concluded from p. 6).

Eclogite Boulders without Diamonds.

3. PART of a boulder, which must have been about a foot in diameter.—In macroscopic aspect it presents a general resemblance to the rocks described above, with, however, the possibility of a second green constituent. This is not confirmed on microscopic examination. The rock consists, practically, of pyrope and diopside, as already described, except that negative crystals are rather unusually conspicuous in the latter. Into the details of these, as the point seems not to have any bearing on the present investigation, I do not purpose to enter.

4. A fragment, more irregular in form than the others, measures, very roughly, about 7 in. by $4\frac{3}{4}$ in. by $3\frac{1}{2}$ in. It retains a good piece of the outer surface, which, though now a little corroded, was once smooth. The rock, which is rather decomposed and crumbly, consists chiefly of three minerals: garnet, not quite so large, paler and more pink in colour than the last-named; an emerald-green pyroxene, and a yellowish or greenish grey, platy to fibrous mineral, suggestive of a second more altered pyroxene. In thin slices the paler and pinker tint of the garnet is very perceptible, as well as the tendency to a rude and generally parallel cleavage. But we find in it, under the microscope, a few microlithic enclosures, of an apparently colourless mineral, which occurs in long prisms crossed at about 70° by an occasional transverse cleavage, and extinguishing at an angle of about 26° with the longer edge. Many of the cracks exhibit slight decomposition, starting from them, and are sometimes occupied by calcite. The pyroxene, under the microscope, hardly differs from the one already described, except that the green tint is slightly richer and one or two crystals contain the small dark brown negative crystals, common in hypersthene and diallage. The dominant cleavage, as before, is along the clinopinacoid.†

The third mineral proves to be an altered enstatite, but I leave the details for the present as it is better preserved in another rock. A fourth constituent is also present, but more sparingly, viz., a pale brown mica, only moderately pleochroic (phlogophite?). It occurs generally in plates, averaging about 0.1 inch long. The minerals appear to have formed in the following order: (a) garnet, (b) diopside, (c) mica, (d) enstatite. As before, iron oxides are very inconspicuous; there may be a grain or two (small) of serpentinised olivine. The marked presence of enstatite distinguishes this rock from the others, but it differs from the eulysites by the substitution of that mineral for olivine, and so links those rocks to the more ordinary eclogites. The occurrence of a little mica indicates the presence of a small amount of an alkali in the magma. If necessary we may name it newlandite, but personally I should prefer to call it an enstatite-eclogite, for I think the coinage of fresh titles more often a bane than a boon to science.

5. This boulder is almost perfect, except that the general flatness of one side indicates either traces of an old fracture or considerable loss by crumbling. The surface has

been smooth, but it has suffered from unequal weathering of the minerals. Its girth, in three directions at right angles, is approximately $20\frac{1}{2}$ in. by $19\frac{1}{2}$ in. by $17\frac{1}{2}$ in. It appears only to differ from the last-described in having its garnets a shade more purple, and in an approach to a banded structure; the diopside being rather more abundant in a middle zone, the garnet in one, the enstatite in the other of the outer zones. Being satisfied that it is merely a variety of the last-described rock, I have preferred to leave it as an intact boulder.

6. The next fragment, measuring about 3 in. by $2\frac{1}{4}$ in. by 2 in. and retaining part of its smooth outer surface, is labelled "Found in the yellow ground of No. 2 mine,* 50 feet deep." Though it is much more decomposed than the others, the purplish garnet, the emerald-green pyroxene, the altered enstatite (here very rotten), and a flake or two of phlogophite (?) are easily made out. It is obviously a more decomposed specimen of the rock represented by the two preceding specimens.

7. The last of this group of specimens is a rock fragment,† measuring about $3\frac{1}{2}$ in. by 2 in. in length and breadth, and slightly exceeding an inch in greatest thickness. Its outline is irregular, being determined by the fracture of the predominant diallage-like mineral. The crystals of this run large, an inch or more in length, breadth, and thickness. It is greyish-green in colour, having one dominant cleavage, with a sub-metallic lustre, and close subordinate cleavages, giving a somewhat fibrous aspect to that surface. Between these large crystalline lumps, numerous small, ill-defined garnets (pyrope) seem crowded, so as to form fairly continuous partings, generally hardly 0.1 inch in thickness. As the readiness with which the rather soft pyroxenic constituent split away made it improbable that a good slice could be cut, and I was reluctant to injure the specimen, I contented myself with detaching a few flakes of this constituent for microscopic work, since the determination of its identity was sufficient for my purpose. These show the mineral to have one easy cleavage and a rather fibrous structure; they give straight extinction parallel with this. As the usual rings and brushes can be seen on the face of easy cleavage, the mineral belongs to the bastite group. The same is true of the enstatite in boulder (4), though, as it is slightly more fibrous, and not in quite so good a condition, the optical picture is less distinct. Thus we may name the rock from which the present specimen has been broken, a garnet-bearing bastitite.

8. This specimen, said to be a fragment of a boulder, is very different from the rest. It is a compact greenish grey rock containing enclosures, which give it the aspect, at first sight, of a pebbly mudstone. Microscopic examination shows it to be a compact felspathic diabase, with vesicles, which have been filled up with calcite, chlorites, and other secondary minerals (probably zeolites), but not to have any special interest. Its relations appear to be with the rocks occurring in a conglomerate which we shall mention in a later paragraph.

The "Blue Ground" and Associated Rocks.

Two areas of diamantiferous rock are now being worked at the Newlands Mines. The shape of the one which supplied most of the specimens described in this paper is irregular, and, so far as I know, exceptional. Its outline at the surface may be roughly compared to a rounded triangle into the base of which the point of a rather short shuttle is thrust, the greatest breadth of the two being about equal. Exploratory workings at a depth of 300 feet show that the former area rather quickly narrows, and the latter terminates in clefts; the "blue ground," in fact, appears to fill a fissure, broadening in two places to vents which have been traced for some distance underground southwards from the principal mass of

* A Paper read before the Royal Society, June 1, 1899.

† As noticed by Professor Lewis, *ut supra*, p. 22, in the diopside, the prism cleavage has practically disappeared, and a clinopinacoidal cleavage replaces the orthopinacoidal usual in diallage.

* The others come from another mine (No. 1).

† I am informed that this was not part of a boulder, but came out of the "blue ground" nearly in its present condition.

diamantiferous rock, as represented in the annexed section.

An igneous rock occurs on either side. It is compact, a greenish grey in colour, not unlike some of the less acid Welsh felstones. Under the microscope it is found to be much affected by secondary mineral changes: the iron oxides alone being in good preservation. A few small crystals of decomposed felspar are scattered in a yet more decomposed matrix, of which the minor details are uninteresting. The rock may be classed with the compact, rather felspathic, diabases. These, farther to the south, turn off rather sharply to east and west.

In the interval, about 12 feet in width, between walls of this diabase, ribs of the "blue" and a mudstone alternate, the thickest one of the former being from 3 to 4 feet in width, and the inner part of it is in better preservation than the outer. Specimens have been examined from the heart of the mass (vii), a part outside it (vi), and the exterior portion (v). The first (vii) in texture, hardness, and colour, reminds me a little of the dark serpentine found north of Cadgwith, in Cornwall. In this matrix roundish spots occur, some darker than it, others a yellow-green colour, besides a few angular whitish spots. The block is traversed by two or three thin calcareous veins. Specimen (vi), while generally similar, is more decomposed, and apparently contains some fragments of

the interior (on the whole the best preserved rock) it is locally assuming a green colour, no doubt by hydration. In the specimens from the thick rib, the one last named contains mineral grains and rock fragments, except for a few flakes of the usual mica. The former are a mixture of two fibrous minerals, the larger part corresponding with actinolite; the rest, giving lower polarisation tints, may be serpentine. This fact, and structures suggestive of the former presence of a cleavage more regular than that of olivine, make it more probable that diopside was the original mineral. Though iron oxide is present in specks and rods (especially in the worst preserved specimen), this occurs either in the outer part, or as though it had been deposited along cleavage planes. In the thin rib of "blue" (iii) some of the grains are composed partly of a fibrous mineral, as above described, and partly of a clear one, which often affords rather rich polarisation tints, and presents some resemblance to quartz. Its precise nature is difficult to determine, owing to the absence of distinctive characters, but I believe it to be of secondary origin. Rock fragments are not common in the first (interior) specimen (vii); one, however, is probably an altered shale, and another possibly a limestone. This is bordered by a pale pyroxenic mineral piercing into the grains of calcite. In the second specimen (vi) fragments are rather common; among them are those of diabase,

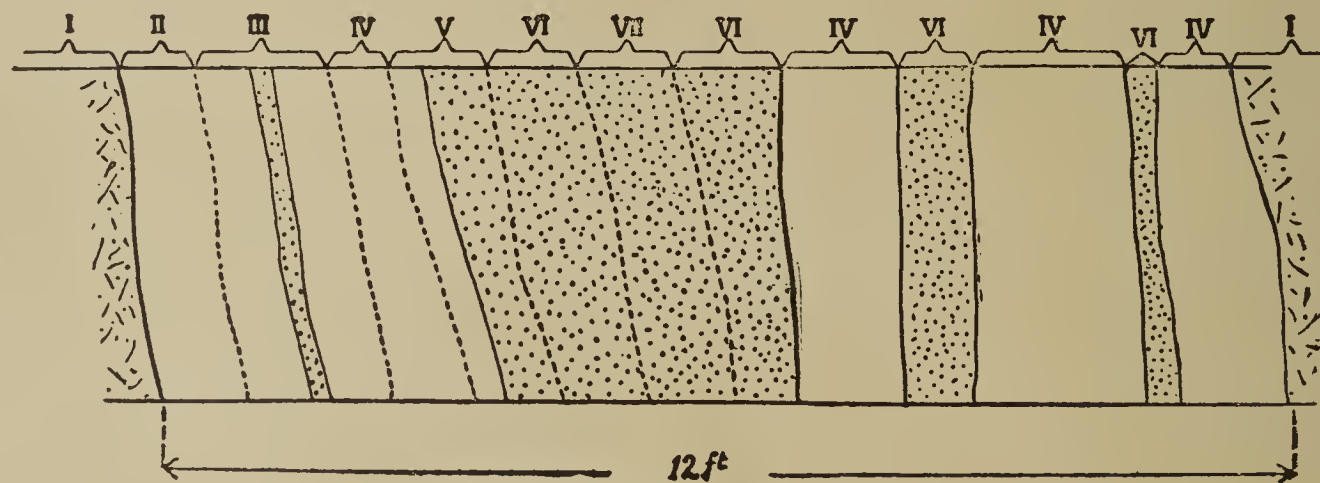


FIG. 3.

shale. Specimen (v) has a stratified aspect, being a dull grey faintly mottled rock, with streaky, dark, rather carbonaceous-looking bands; the origin being doubtful, till it is seen under the microscope. A fourth specimen (iii) shows the mudstone traversed by a vein of rather pale-coloured decomposed "blue," not exceeding an inch in thickness. A fifth (ii) is from near the diabase on the western side, a dark compact rock, faintly mottled, here and there presenting a slight resemblance to a "blue" traversed by thin veins of a carbonate; and sixth (iv) from a like position on the opposite side is a generally similar rock, but with wider veins filled with more coarsely crystalline calcite. The last specimen represents the "blue" in the "neck," a few yards to the north and at the same level (300 feet). This, inferior in preservation to the first-named, includes numerous rounded fragments a little darker than the matrix, with others, angular to subangular, some also darker and some lighter than it.

A brief summary of the results of microscopic examination may suffice, as these rocks do not materially differ from specimens obtained in the De Beers mine, of which I have published a full account (*Geol. Mag.*, 1895, p. 492, and 1897, p. 448).

The matrix is a mixture, in slightly variable quantities, of granules of calcite or dolomite, serpentine, pyroxene, and iron oxides, in which occur flakes with fairly idiomorphic outlines of a warm-brown mica, moderately pleochroic, corresponding with that described (*Geol. Mag.*, 1897, pp. 450, 451) in one or two specimens from De Beers Mine. The prisms are about 0.002 inch in diameter, and sometimes nearly as thick. This mica, which, as stated in a former paper, I consider a secondary product, occurs abundantly in all the specimens, but in that from

ranging from fine to coarse, one specimen of the latter, originally, perhaps, an inch in diameter, showing an ophitic structure; felspar and augite both being rather altered, seemingly by infiltration, and one small fragment resembles a subcrystalline limestone. Specimen (v) does not materially differ, but seems to contain more carbonate than the others. The dark streaking is due to grains of iron oxide or serpentine with much opacite; rock fragments few and small. Specimen (iii) from the thin vein contains a very few small rock fragments, mudstone, or shale, more or less altered, possibly also a compact diabase. The "country rock" is a mudstone, consisting of small chips of quartz and felspar, variable in size, embedded in a dusty matrix, including a carbonate, which is more abundant within about a fiftieth of an inch from the junction. The part is slightly stained, but I was unable to detect any signs of contact metamorphism. Specimens (ii) and (iv) are generally similar, but the former contains some small rounded bits of varieties of diabase, and one may represent a crystalline limestone. The veins are filled with calcite and other secondary products, and are bordered by a very thin film of a brown micaceous mineral, like that described as often permeating the "blue." Both specimens suggest micro-mineralogical changes, such as might be produced by the passage of hot water.

Other specimens of the sedimentary rock in the immediate neighbourhood of the blue have been forwarded to me by Mr. Trubenbach, one, from the adit on the southern side of the section mentioned above, is a grey mudstone, containing a flattish rectangular pebble, of a dark green compact rock. Two others are from No. 2 mine, or about 700 yards to the south-west. One, struck in the shaft at a depth of 200 feet, is a conglomerate,

composed of well-rounded rock fragments, with some scattered grains of quartz. Each of the former is bordered by a zone of a crystalline carbonate (impure calcite), and the interstices are filled, sometimes by a clearer variety of the same, but more often by some minutely granular secondary product. Of the rock fragments, one is a sub-crystalline dolomitic limestone; two, perhaps, are chalcedony; the remainder are igneous; the majority being varieties of diabase, sometimes rather decomposed; the rest trachytes, mainly andesites. Their general aspect and the not unfrequent presence of vesicles (now filled with viridite) suggests that they have been furnished by lava-flows. Another specimen, obtained in the same working at a depth of 400 feet, is a rather felspathic diabase, not unlike one of the varieties in the conglomerate. It is a good deal decomposed, is not improbably from a lava-flow, but does not call for a minute description.

Conclusion.

Thus the diamond has been traced up to an igneous rock. The "blue ground" is not the birthplace either of it or of the garnets, pyroxenes, olivine, and other minerals, more or less fragmental, which it incorporates. The diamond is a constituent of the eclogite, just as much as a zircon may be a constituent of a granite or a syenite. Its regular form suggests not only that it was the first mineral to crystallise in the magma, but also a further possibility. Though the occurrence of diamonds in rocks with a high percentage of silica (itacolumite, granite, &c.) has been asserted, the statement needs corroboration. This form of crystallised carbon hitherto has been found only in meteoric iron (Canyon Diablo), and has been produced artificially by Moissan and others with the same metal as matrix. But in eclogite the silica percentage is at least as high as in dolerite; hence it is difficult to understand how so small an amount of carbon escaped oxidation. I had always expected that a peridotite (as supposed by Professor Lewis), if not a material yet more basic, would prove to be the birth-place of the diamond. Can it possibly be a derivative mineral, even in the eclogite? Had it already crystallised out of a more basic magma,* which, however, was still molten, when one more acid was injected, and the mixture became such as to form eclogite? But I content myself with indicating a difficulty, and suggesting a possibility; the fact itself is indisputable: that the diamond occurs, though rather sporadically, as a constituent of an eclogite, which rock, according to the ordinary rules of inference, must be regarded as its birth-place.

This discovery closes another controversy, viz., that concerning the nature of the "Hard blue" of the miners (Kimberlite of Professor Lewis), in which the diamond is usually found. The boulders described in this paper are truly water worn. The idea that they have been rounded by a sort of "cup and ball" game played by a volcano may be dismissed as practically impossible. Any such process would take a long time, but the absence of true scoria implies that the explosive phase was a brief one. They resemble stones which have travelled for several miles down a mountain torrent, and must have been derived from a coarse conglomerate, manufactured by either a strong stream or the waves of a sea from fragments obtained from more ancient crystalline rocks.† The "washings,"‡ a parcel of which I received from Mr. Trubenbach, also show that the boulders are really water worn. Besides two unworn pieces of pyrite and a rough

bit of eclogite, about three-quarters of an inch in diameter, the pyroxenic constituent of which was a bright emerald green (? smaragdite), I find part of a subangular fragment of chrome-diopside associated with two or three flakes of the usual mica, a well rounded garnet fully 0.6 inch across, and half a well worn pebble of eclogite, about one inch long and half an inch thick. The rounded water-worn look of the great majority of the smaller constituents (chiefly garnets and pyroxenes), about the size of hemp seed, is very obvious. I had suspected some of the grains washings from the De Beers Mines to have been similarly treated; but here it is indubitable, indeed many of the dark green specimens are so smooth outside that they could only be identified after fracture. The ordinary diopside can, however, be recognised, with some of a clearer and brighter green. Most of the garnets are pyropes, but a few resemble essonite. I find also some grains of iron oxide and of vein quartz. Thus, the presence of water-worn fragments, large and small, in considerable abundance, shows the "blue ground" to be a true breccia, produced by the destruction of various rocks (some of them crystalline, others sedimentary, but occasionally including water-worn boulders of the former)—i.e., a result of shattering explosions, followed by solfataric action. Hence the name Kimberlite must disappear from the list of the peridotites, and even from petrological literature, unless it be retained for this remarkable type of breccia.

Boulders, such as we have described, might be expected to occur at the base of the sedimentary series, in proximity to a crystalline floor. The Karoo beds in South Africa, as is well known, are underlain in many places by a coarse conglomerate of considerable thickness and great extent, called the Dwyka conglomerate, which is supposed to be Permian or Permo-carboniferous in age. It crops out from beneath the Karoo beds at no great distance from the diamond-bearing district, and very probably extends beneath it. If this deposit has supplied the boulders, the date of the genesis of the diamond is carried back, at the very least, to Palæozoic ages, and possibly to a still earlier era in the earth's history.

NOTE ON THE ACTION OF LIQUID HYDRIODIC ACID ON ETHYL ETHER.*

By F. G. COTTRELL and ROY RAVONE ROGERS.

SOME time ago, while examining the properties of liquid hydriodic acid (Norris and Cottrell, *Am. Chem. Journ.*, 1896, xviii., 103), it was noted that when the acid was mixed with ether a vigorous action occurred, the temperature rising rapidly, the mixture, which at first appeared to be homogeneous, separated into two layers, one of which was assumed to be ethyl iodide, judging from its appearance and odour, and the other was assumed to be water and the excess of acid. No attempt was made at the time to separate and purify the product, or to determine the yield. The following supplements the previous work in this particular.

The hydriodic acid was prepared and dried according to the method described in the previous paper (*loc. cit.*). The ether was prepared by washing commercial ether with a considerable volume of water, digesting with quicklime for a few days, and distilling from the same. This was again distilled, and then gave a boiling-point constant within a tenth of a degree.

After several preliminary experiments the following form of apparatus was adopted. We believe it will be found a very convenient form for reactions which are to be carried out under pressure.

The sealed end of a straight eudiometer-tube provided

* This, however, cannot have been very rich in iron, because diopside does not contain much of that constituent.

† As these eclogites are very coarsely crystalline, we are justified in assuming they were once deep-seated rocks, and so much more ancient than the date of the conglomerate. To prevent any misunderstanding I may repeat that the matrix from which these boulders were taken (at various depths, from nearly 100 to about 300 feet) cannot be any alluvial deposit, but is the typical "blue ground," practically identical with that in the Kimberley mines.

‡ The name is given to the mineral residue left after washing away the decomposed matrix of the "blue ground."

* Contributions from the Chemical Laboratory of the University of California. From the *American Chemical Journal*, xxi., No. 1.

with a glass stop-cock was cut off, and a smaller tube, sealed at one end, introduced into it, open end first. The cut end of the large tube was then sealed, thus providing a vessel of two chambers, into each of which liquids could be introduced through the stop-cock.

The whole apparatus was now weighed, the tube was then surrounded with solid carbon dioxide, and gaseous hydriodic acid conducted by means of a narrow delivery-tube to the bottom of the eudiometer-tube, where it condensed to a liquid surrounding the inner tube. When about 15 c.c. of this liquid had been collected, the delivery tube was withdrawn, and the acid cooled until it solidified. Then a weighed amount of ether was run into the inner tube, and the stop-cock closed, and tied in securely.

The apparatus was now tipped slightly so that the ether mixed in small quantities at a time with the acid. The ether on coming in contact with the solid acid produced a vigorous reaction. The latter melted rapidly, even while surrounded by the solid carbon dioxide. If the ether and acid are suddenly mixed the temperature will rise from the freezing-point of the acid ($-55^{\circ}\text{C}.$) to at least $+40^{\circ}$ or 50° . When mixing was complete the whole apparatus was weighed to determine the weight of acid used.

During the mixing the products began to separate into two layers. The tube was set aside for a week in a dark place (average temperature about 18°), at the end of which time the heavier of the two layers had relatively increased in volume. After being cooled down somewhat, the tube was opened. Water was added, which mixed with the upper layer, but would not mix with the lower. The lower layer was washed with water, then with a little weak solution of caustic potash, dried over calcium chloride, and distilled twice. The following are the numerical data:—

	Grms.
Weight of ether used.. .. .	8.91
Weight of acid used	42.30

This is 1.33 times the quantity of acid required by theory for the reaction $(\text{C}_2\text{H}_5)_2\text{O} + 2\text{HI} = 2\text{C}_2\text{H}_5\text{I} + \text{H}_2\text{O}$.

Weight of crude product after washing with water, 35 grms.; this is 94 per cent of the quantity required by theory.

Weight of product after first distillation, 32.8 grms., which is 88 per cent of the quantity required by theory.

After the second distillation the whole of the material boiled between 71.9° and 72° under 756 m.m. pressure. The boiling-point of ethyl iodide, given by different authorities (Landolt and Börnstein, *Chem. Phys. Tab.*, 1894, p. 65), ranges about a degree on each side of this. Its specific gravity at 18° referred to water at the same temperature was found to be 1.941. Hagen gives 1.935 at 20° , and Linnemann 1.944 at 14.5° (*loc. cit.*). Its refractive index for the D line was 1.5133 at 18.5° . Hagen (*loc. cit.*, p. 427), gives 1.5131 at 20° .

Silva (*Compt. Rend.*, 1875, lxxxi., 323), found that when gaseous hydriodic acid reacted on methyl ether at 0° to 4° , the whole of the ether was converted into methyl iodide. With ethyl ether, on the contrary, only part was converted into iodide and part into alcohol; and the same was true for the higher ethers. No quantitative data are given.

The formation of water by the reaction itself in such cases as the above, soon establishes the same condition as when using a concentrated aqueous solution of the acid. It would be interesting to study the behaviour of the anhydrous acid in reactions where no water can form; e.g., in the addition of hydrogen to benzene (*Cf. Berthelot, Journ. Prakt. Chem.*, 1868, civ., 106).

It seems not improbable from the rapid and widespread increase in our facilities for liquefying and handling considerable quantities of gases that this method of applying such reagents as chlorine, sulphur dioxide, and ammonia may eventually come into quite general use. It has the great advantage of permitting a high concentration of the

reagent without the necessity of introducing water or other solvents, while its practical application is by no means as difficult as might at first be supposed.

THE ELECTROLYTIC SEPARATION OF CADMIUM FROM IRON.

By W. STORTENBECKER.

A METHOD for separating these two metals in slightly acid solution has already been described by Smith. As a cyanide solution gives the best deposits of cadmium the author has made certain experiments with the object of finding out whether such a solution could not be used for the electrolytic separation of iron from cadmium.

When an excess of cyanide of potassium is added to a solution of a ferrous salt, a soluble ferrocyanide of potassium is formed. With solutions of ferric salts, hydrated peroxide of iron is produced, and only a very small proportion of iron passes into the cyanide solution.

The method proposed by the author is based on the non-electrolytic decomposition of the soluble ferrocyanide of potassium.

The mixed salts of iron and cadmium are dissolved in 100 c.c. of water very slightly acidulated with a few drops of dilute sulphuric acid; to this is added 2 or 3 grms. of pure cyanide of potassium, and the whole heated until the solution becomes perfectly clear. If this clarification requires too long a time a few drops of caustic potash may be added. The solution is then diluted to 200–250 c.c., and, after cooling, electrolysed with a current of 0.05 to 0.10 ampère per square decimetre. The deposit of cadmium is perfectly coherent.

If the solution contains but a very small quantity of iron, the floating hydrated peroxide may be neglected; but if, on the contrary, the iron is present in any considerable proportion it becomes necessary to reduce this ferric salt to the ferrous state by means of sulphurous acid; to effect this it suffices to add to the acid solution a small quantity of sulphite of soda, and heat for a short while.—*Zeit. für Elektrochem.*, iv. [17], p. 409.

CARNOTITE: A NEW MINERAL.

By MM. FRIEDEL and CUMENGE.

ONE of us has recently received from America several samples of a new uraniferous mineral. It occurs in the form of a yellow powder or mass easily crumbled between the fingers, which it stains strongly yellow. A preliminary examination showed that this mineral is principally formed, in most samples at any rate though we have had purer ones, of silica in the form of sand. This sand is intimately mixed with a yellowish material consisting of very small grains of which it is impossible to identify the structure, even with a very high power microscope, although it is undoubtedly crystalline, and acts on polarised light.

By repeated levigations a great part, though not the whole, of the sand can be removed. For this reason we preferred to analyse the material as it was, after removing the silica by the action of dilute nitric or hydrochloric acid, which easily dissolved the yellow uraniferous substance. By this means we get with nitric acid a yellow solution, and with hydrochloric acid a beautiful green one.

The mineral contains a certain proportion of water, but it is not advisable to calcine at a bright red heat to effect its determination, as it is very difficult to afterwards dissolve it in acid, and the silica remains brown, the colour taken by the mineral itself after calcination.

We have found that the matter dissolved in nitric acid contains, besides a considerable quantity of uranium, both

vanadic acid, iron, aluminium, and traces of copper, lead, and potassium. We also found that it contains, besides the other minerals of vanadium, a certain proportion of the radiant metals discovered by M. and Madame Curie, but these elements are only met with in very small quantities.

The most convenient manner for conducting the analysis consists in evaporating the nitric solution to dryness on the water-bath with an excess of nitric acid, which must be afterwards driven off; after this the residue is taken up with water and filtered. The nitrate of uranium which is undecomposable under these circumstances passes into the filtrate. The vanadic acid, on the contrary, forms with the nitric acid a compound which is destroyed by evaporation, and becomes insoluble in water, especially when nitrate of ammonia is present.

After well washing the filtrate is again evaporated down with nitric acid. After repeating this operation we get, on the one hand, a solution containing the uranium; and on the other hand, on the filter, a precipitate containing the vanadium accompanied by the iron and aluminium.*

The vanadic acid is separated from the iron and aluminium by treating the precipitate on the same filter, placed for this purpose on a funnel fitted with a stop-cock and closed with an indiarubber stopper, with ammonia.

To obtain the vanadic acid it is sufficient to evaporate and calcine the solution of vanadate of ammonia. The iron will be found on the filter in the state of sesquioxide.

Uranium is precipitated in boiling solution by ammonia, and the precipitation repeated a second time, to separate the potash as completely as possible; there now only remains to evaporate the filtrate with the addition of aqua regia, to destroy the ammoniacal salts, then to add sulphuric acid so as to get the potash into the state of sulphate. We can then evaporate the uranic solution to dryness, and take up with alcohol at 95°, which will dissolve the nitrate of uranium, and leave the nitrate of potassium undissolved. Nevertheless, this latter process has not given such good results as the first one.

We have by this means obtained figures leading to the formula $2\text{U}_2\text{O}_3 \cdot \text{V}_2\text{O}_5 \cdot \text{K}_2\text{O} \cdot 3\text{H}_2\text{O}$.

This requires:—

U_2O_3	63.54
V_2O_5	20.12
K_2O	10.37
H_2O	5.95
						99.98

We found.—

U_2O_3	64.70	62.46
V_2O_5	20.31	19.95
K_2O	10.95	11.09
Fe_2O_3	0.96	0.65
H_2O	5.19—4.81		5.19—4.81

The proportion of iron is rather variable; we further noticed on different samples that the sesquioxide of iron forms irregularly divided veins. As for the silica it varies as much as from 10 to 60 per cent, and even more. In an exceptional sample there was only 1.3 per cent, and in another only 7.8 per cent. As for the water the amount has not been definitely determined; we began with the simply air-dried mineral, and found that the quantity present was less than that required by the formula.

However that may be, though, it is clear that we have to deal with a new mineral which constitutes a well defined species. We propose to dedicate it to M. Adolphe Carnot, Member of the Institute, Inspector General of Mines, whose works on mineral analysis are so well known, and who has recently ("Nouvelle

* A slight difficulty occurs when we want to transfer the vanadic acid to the filter. A small portion remains obstinately attached to the porcelain crucible, and we are obliged to re-dissolve it in dilute nitric acid, and evaporate again to dryness. After two or three similar operations we can eventually get practically all the vanadic acid collected on the filter.

Méthode d'Analyse Minérale," p. 55), described, for the estimation of vanadium, the precipitation of the acid in the form of a vanadate of uranium, the formula of which has some analogy with that of the compound we have just described.

This mineral was discovered by M. Charles Poulot, a French chemist, at present living at Denver, in Colorado. He happened to be in the county of Montrose (Colorado), in one of the cavities or pools in the grit-stone rock, which is accompanied by chessylite and malachite. From this source about 10 tons of the mineral was extracted. M. Poulot there recognised the presence of vanadium.

As to the radioactive minerals contained in carnotite, we here give the results found by M. and Madame P. Curie, with their permission.

A sample containing 54 per cent of silica had an activity of 1.25; another much purer and hardly containing any silica, 2.6. The insoluble sulphates mixed with barium and radium, 35; the raw sulphides, 11; finally the sulphides of bismuth and polonium from 50 to 60; the quantity was so small that the results were very uncertain. The activity of uranium was taken as unity.—*Bull. Soc. Chim.*, Series 3, xxi., No. 7.

ON THE HYDROSULPHITES OF AMMONIUM.

By MAURICE PRUD'HOMME.

THE treatment of bisulphite of soda by zinc according to Schützenberger's method, gives rise to the formation of acid hydrosulphite of sodium according to the equation, $3\text{SO}_3\text{NaH} + \text{Zn} = \text{SO}_2\text{NaH} + \text{SO}_3\text{Na}_2 + \text{SO}_3\text{Zn} + \text{H}_2\text{O}$. Of the three molecules of bisulphite present, one only is transformed into hydrosulphite.

Neutral Hydrosulphite of Ammonium.—This can be obtained directly by treating the neutral sulphite of ammonium with zinc.

Like the ammoniacal salts in general this sulphite is transformed in the presence of zinc, into a double salt of zinc and ammonium, with the disengagement of hydrogen, $\text{SO}_3(\text{NH}_4)_2 + \text{Zn} = \text{SO}_3\text{Zn} \cdot 2\text{NH}_3 + \text{H}_2$. The nascent hydrogen, reacting on a second molecule of the sulphite, converts it into hydrosulphite $\text{SO}_3(\text{NH}_4)_2 + \text{H}_2 = \text{SO}_2(\text{NH}_4)_2 + \text{H}_2\text{O}$.

Practically we start with commercial bisulphite of ammonium at 28° B., which must be saturated with NH_3 (100 bisulphite, 20 to 25 ammonia). After cooling we fill with it a flask containing zinc turnings. The flask, properly corked, is alternately shaken to renew the surfaces of contact, and cooled in a current of water. At the end of about ten minutes the reaction is finished. An abundant white deposit of the double sulphite of zinc and ammonium is formed. It is allowed to stand another quarter of an hour, and then filtered. Under these conditions of concentration the filtrate does not contain any zinc.

When treated with permanganate of potash, acidulated with sulphuric acid, it has practically the same reducing power as the neutral sulphite originally taken. The return is about 96 to 98 per cent of theory.

Of the two molecules of sulphite of ammonium present one has been converted into a double sulphite of zinc and ammonium, and the other into hydrosulphite of ammonium.

From the laboratory point of view, this process has the following advantages over that with bisulphite of soda.

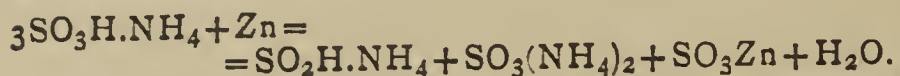
1. Greater stability and greater concentration of the product.

2. Easy purification by simple filtrations. (In the bisulphite of soda process the sulphates of Na and Zn must be removed by lime).

3. Hydrosulphite of ammonium is very suitable for the preparation of other hydrosulphites.

This same reaction applied to the hyposulphite, hyposulphate, and trithionate of ammonia has only given negative results.

Acid Hydrosulphite of Ammonium.—When we attempt to prepare the acid hydrosulphite of ammonium by means of bisulphite of ammonium and zinc, we observe the almost immediate formation of a white precipitate, which is not produced in the preparation of the acid hydrosulphite of soda. The explanation of this phenomenon is found in the facts just made known. In a first phase the reaction takes place with the bisulphite of ammonium, as with the sodium—



The neutral sulphite of ammonia formed, itself enters into the reaction—



so that, starting with 6 molecules of bisulphite of ammonium, we finally obtain 2 molecules of acid hydrosulphite, 1 molecule of neutral hydrosulphite, 2 molecules of sulphite of zinc, and 1 molecule of double sulphite of zinc and ammonium. The half of the bisulphite is thus again transformed in this case into hydrosulphite.—*Bull. Soc. Chim.*, Series 3, xxi., No 7.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

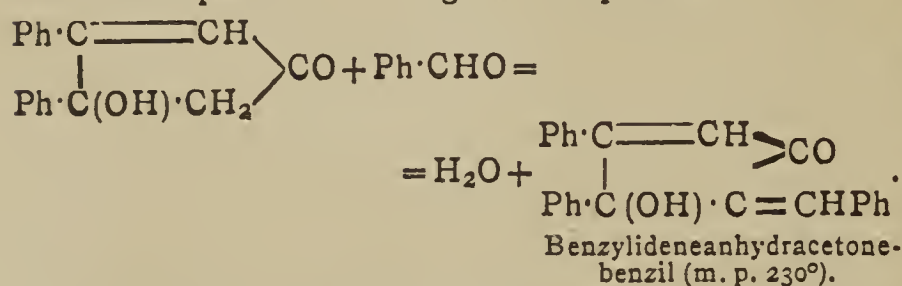
Ordinary Meeting, June 15th, 1899.

Professor T. E. THORPE, F.R.S., President, in the Chair.

(Continued from p. 10).

91. "Condensations of Anhydracetonebenzil and its Analogues with Aldehydes." By FRANCIS R. JAPP, F.R.S., and ALEXANDER FINDLAY, M.A., B.Sc.

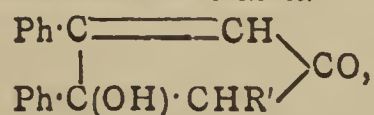
The authors find that anhydracetonebenzil (diphenylcyclopentenolone) and benzaldehyde interact in presence of alcoholic potash according to the equation—



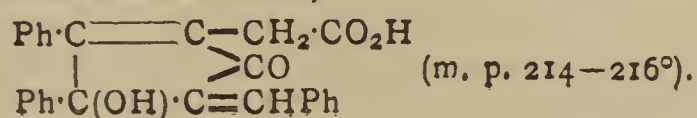
In like manner, by acting on anhydracetonebenzil with cuminaldehyde, they obtained *cumylideneanhydracetonebenzil*, $\text{C}_{27}\text{H}_{24}\text{O}_2$ (m. p. 148°); and with cinnamaldehyde, *cinnamylideneanhydracetonebenzil*, $\text{C}_{26}\text{H}_{20}\text{O}_2$ (m. p. 222°).

By reduction with hydriodic acid, benzylideneanhydracetonebenzil yields a compound $\text{C}_{24}\text{H}_{18}\text{O}$ (m. p. 182°)—probably a *benzylidenediphenylcyclopentenone*.

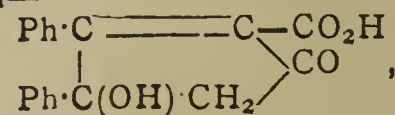
The authors have applied the interaction with benzaldehyde to determining the constitution of the monosubstitution derivatives of anhydracetonebenzil, in which there is a doubt as to whether the substitution occurs in the CH- or in the CH₂-group. The condensation cannot occur except in the case of derivatives containing the CH₂-group intact. Thus Japp and Lander assigned to the monalkyl derivatives the formula—



and in accordance with this, it was found that amylanhydracetonebenzil does not interact with benzaldehyde. On the other hand, α -anhydrobenzillævulic (α -anhydracetonebenzilethylol) acid, in accordance with the formula ascribed to it by Japp and Murray, gives *benzylidene- α -anhydrobenzillævulic acid*,—

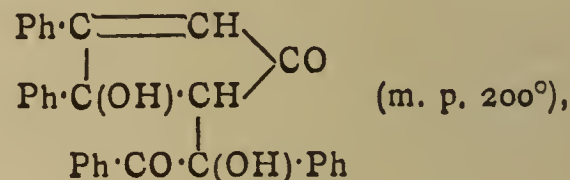


Anhydracetonebenzilcarboxylic acid, however, must have the constitution—



instead of the alternative constitution adopted for it by Japp and Lander, inasmuch as it yields a benzylidene derivative, $\text{C}_{25}\text{H}_{18}\text{O}_4$ (m. p. about 245°).

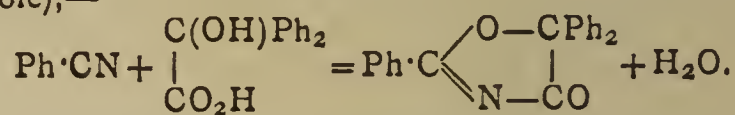
Anhydracetonebenzil and benzil interact in presence of alcoholic potash to form an aldol condensation compound,—



identical with anhydracetonedibenzil, previously obtained by the condensation of acetone with excess of benzil (*Trans.*, 1885, xlvii., 33). The hitherto unknown constitution of anhydracetonedibenzil is thus ascertained.

92. "Triphenyloxazolone." By FRANCIS R. JAPP, F.R.S., and ALEXANDER FINDLAY, M.A., B.Sc.

By the action of cold concentrated sulphuric acid on a mixture of benzonitrile and benzoic acid, the authors have obtained *triphenyloxazolone* (triphenylketodihydrooxazole),—



It crystallises in large, transparent rhombs melting at 136°. At the same time, *benzimidoxydiphenylacetic acid*, $\text{Ph}\cdot\text{C}(\text{NH})\cdot\text{O}\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$, is formed, which is deposited from its solutions in prisms or plates melting at 190°.

Heating with acetic anhydride converts the acid into the oxazolone, whilst boiling with dilute potash transforms the oxazolone into a salt of the acid.

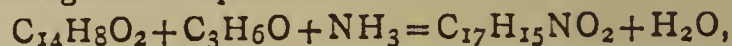
When the acid is heated with strong potash, it parts with carbon dioxide, and yields *benzimidobenzhydrylic oxide*, $\text{Ph}\cdot\text{C}(\text{NH})\cdot\text{O}\cdot\text{CHPh}_2$ (needles, m. p. 172–173°). The constitution of the latter compound was proved by its synthesis from benzonitrile and benzhydrol under the influence of gaseous hydrogen chloride. It thus belongs to the class of imido-ethers described by Pinner and Klein (*Ber.*, 1877, x., 1889).

Both the oxazolone and the acid, when boiled for a few minutes with fuming hydriodic acid, yield benzamide and diphenylacetic acid. Under the same conditions, benzimidobenzhydrylic oxide gives diphenylmethane in place of diphenylacetic acid.

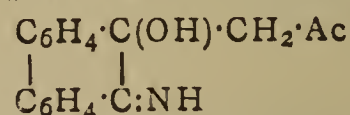
None of the other nitriles and α -hydroxy-acids with which the authors experimented yielded compounds corresponding with the foregoing.

93. "Interaction of Phenanthraquinone, Acetophenone, and Ammonia." By FRANCIS R. JAPP, F.R.S., and ANDREW N. MELDRUM, B.Sc.

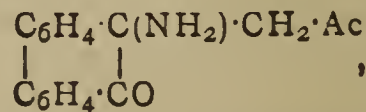
Japp and Streatfeild showed (*Trans.*, 1882, xli, 270) that phenanthraquinone, acetone, and ammonia interact according to the equation—



and to the compound thus formed the constitution—

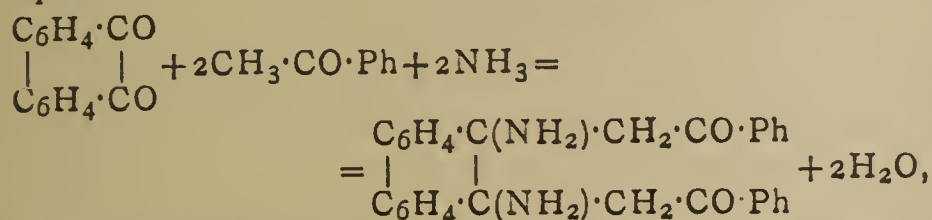


was assigned by Japp and Miller (*Trans.*, 1885, xlvii., 12). The results of the present investigation, however, render the constitution—



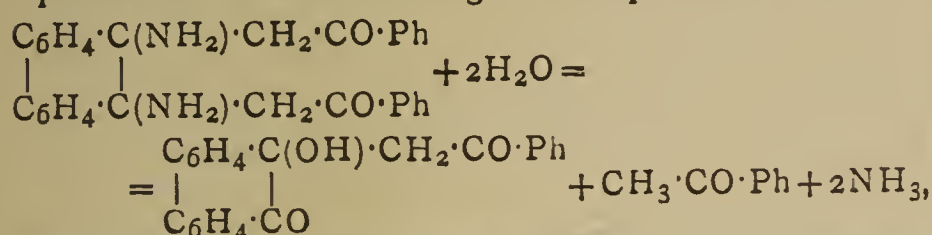
analogous to that of diacetoneamine, more probable. The compound may be named *acetonylaminophenanthrone*.

Thus the authors find that phenanthraquinone, acetophenone, and alcoholic ammonia interact according to the equation—



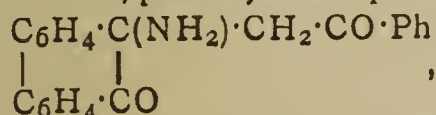
yielding *diphenacyldiaminodihydrophenanthrene*, which crystallises in colourless, silky needles, and decomposes about 150° without showing a definite melting point. It is evident that a constitution analogous to that ascribed by Japp and Miller to the acetone-ammonia derivative of phenanthraquinone is not possible in the case of this compound.

The acetophenone-ammonia derivative is hydrolysed by aqueous oxalic acid according to the equation—



yielding *phenacylhydroxyphenanthrone* (*acetophenone-phenanthraquinone*), which crystallises in small prisms or six-sided plates melting with decomposition at 125—130°.

By the interaction of phenanthraquinone acetophenone, and aqueous ammonia, *phenacylaminophenanthrone*—



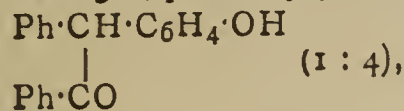
analogous to the acetone-ammonia derivative, was obtained. It crystallises in minute, colourless, six-sided plates melting about 160° with decomposition and evolution of gas. A substance, apparently identical with the foregoing, was obtained by the action of the ammonia on phenacylhydroxyphenanthrone.

The ease with which these compounds break up into their generating substances renders a detailed study of their constitution impossible.

Other ketones, such as methyl ethyl ketone and diethyl ketone, appeared to interact in a similar manner with phenanthraquinone and ammonia; but it was found impossible to obtain the resulting compounds in a state of purity.

94. "*Furfuran Derivatives from Benzoin and Phenols.*" By FRANCIS R. JAPP, F.R.S., and ANDREW N. MELDRUM, B.Sc.

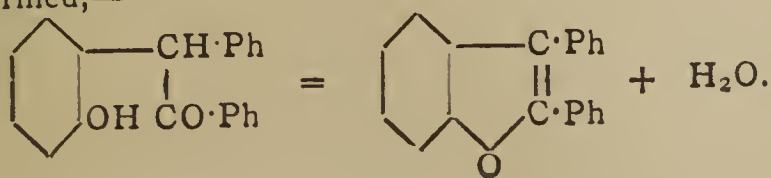
By the action of cold, concentrated sulphuric acid on a mixture of benzoin and phenol, Japp and Wadsworth (*Trans.*, 1890, lviii., 965) obtained paradesylphenol-sulphonic acid, from which, by hydrolysing it with strong hydrochloric acid at 150°, paradesylphenol,—



was prepared.

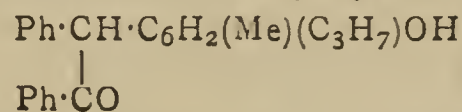
The authors find that, by heating a mixture of benzoin and phenol with sulphuric acid of 73 per cent strength, the foregoing condensation occurs without subsequent sulphonation of the resulting compound, and an excellent yield of paradesylphenol is obtained. The various condensations described in this note were effected by means of a sulphuric acid of this strength.

If the desyl-group were to take up the ortho-position towards the hydroxyl of the phenol, it is evident that, by a further elimination of water, a furfuran derivative might be formed,—

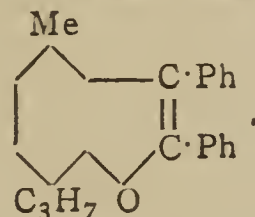


With phenol and benzoin, no such reaction occurs; the para-compound alone is formed. With thymol and benzoin, however, a mixture of desylthymol and cymodiphenylfurfuran is obtained. In the case of resorcinol and of quinol, either one or two diphenylfurfuran groups may be introduced. With phloroglucinol, only the compound containing three such groups was obtained.

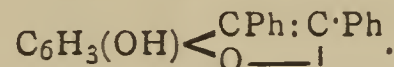
The following compounds have been prepared: (1) From thymol and benzoin. *Desylthymol*,—



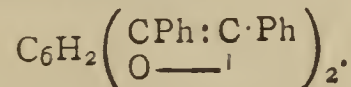
Laminæ melting at 126°. The acetyl derivative forms needles melting at 110°. The position of the desyl group in desylthymol is uncertain, except that it is not adjacent to the hydroxyl group. *Cymodiphenylfurfuran*—



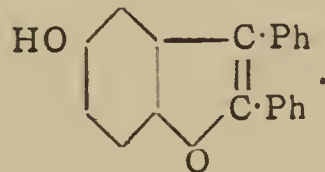
Slender needles melting at 115—116°. (2) From resorcinol and benzoin. *Metahydroxybenzodiphenylfurfuran*,—



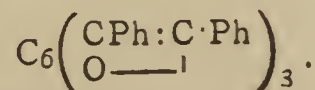
Slender needles, with satiny lustre, melting at 117.5°. The acetyl derivative crystallises in slender prisms, melting at 117°. The practical coincidence in the melting points of these two substances is anomalous. They differ greatly in their other physical properties. *Meta-benzotetraphenyldifurfuran*,—



Slender needles, melting at 217—219°. Solutions show a violet fluorescence. Two constitutions, between which it is at present impossible to decide, might be assigned to each of these derivatives. Isomeric forms were not observed. (3) From quinol and benzoin. *Parahydroxybenzodiphenyldifurfuran*,—



Flat needles, melting at 158—160°. The acetyl derivative forms laminæ melting at 137°. *Parabenzotetraphenyldifurfuran*, $\text{C}_{34}\text{H}_{22}\text{O}_2$. Constitution analogous to that of the corresponding resorcinol derivative. Only one of the two possible isomerides observed. Needles melting at 278°. Solutions strongly fluorescent; crystals slightly so. (4) From phloroglucinol and benzoin. *Benzohexaphenyiltrifurfuran*,—



Slender needles, melting at 360°.

The foregoing work was completed last year, before the publication of Græbe's investigation of benzoin yellow (*Ber.*, 1898, xxxi., 2975), in which it is shown that, by the action of sulphuric acid on a mixture of benzoin and gallic acid, a compound containing a diphenylfurfuran group is formed.

95. "*Interaction of Benzoin with Phenylenediamines.*" By FRANCIS R. JAPP, F.R.S., and ANDREW N. MELDRUM, B.Sc.

By heating benzoin with aniline and a little aniline hydrochloride, Japp and Murray (*Trans.*, 1894, lxx., 892), obtained 2':3'-diphenylindole. The desylanilide, $\text{Ph}\cdot\text{CO}\cdot\text{CH}(\text{NH}\cdot\text{Ph})\cdot\text{Ph}$, which is formed in the first instance, parts with water, under the influence of the

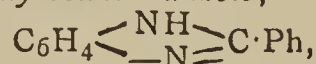
hydrochloric acid, yielding the indole. The authors have now studied this reaction with the phenylenediamines, in order, if possible, to obtain the corresponding benzodipyrrole derivatives. Only in the case of metaphenylenediamine, however, did the reaction take place in the desired sense.

Benzoin, heated with metaphenylenediamine and a little of its hydrochloride, gave *metabenzotetraphenyldipyrrole*,—

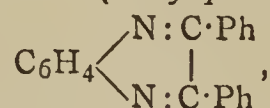


which forms slender needles melting at 282°. Two constitutions are possible for this compound, and at present there is apparently no means of deciding between them. Substituting paraphenylenediamine and its hydrochloride for the meta-compounds in the foregoing reaction *bidesylparaphenylenediamine*, $\text{C}_6\text{H}_4(\text{NH}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{Ph})_2$, was obtained in the form of bright yellow, minute laminae melting at 257°. It yields a diacetyl derivative crystallising in slender, colourless needles melting at 279°. By heating either bidesylparaphenylenediamine or its diacetyl derivative with zinc chloride, or by heating benzoin with paraphenylenediamine hydrochloride alone, indications of the formation of a benzodipyrrole derivative were obtained; but the compound was not formed in quantity sufficient to admit of its purification.

By heating benzoin with orthophenylenediamine hydrochloride, *phenylbenzimidazole*,—



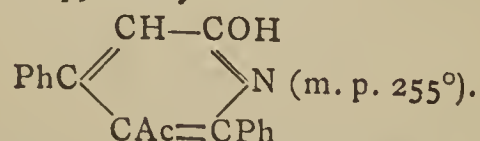
was obtained, the benzoin molecule breaking up in the process. Benzoin and free orthophenylenediamine, on the other hand, yielded *diphenylquinoxaline*,—



oxidation taking place during the process. The formation of the latter compound in this reaction had, as we afterwards found, been already observed by O. Fischer (*Ber.*, 1891, xxiv., 720).

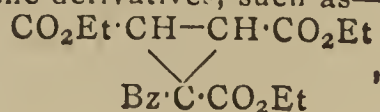
96. "The Condensation of Ethyl Salts of Acids of the Acetylene Series with Ketonic Compounds." By SIEGFRIED RUHEMANN and A. V. CUNNINGTON.

The substitution products of ethyl phenylpropionate, *e.g.*, ethyl *p*-nitrophenylpropionate, on treatment with sodium ethoxide, yield, with ethyl acetoacetate and ethyl benzoylacetate respectively, the nitro-substituted cyclic compounds corresponding to the α -pyrone derivatives previously described. The homologues of ethyl acetoacetate, however, on treatment with ethyl phenylpropionate and sodium ethoxide, give rise to a mixture of compounds which the authors were unable to separate by fractional distillation. The α -pyrone derivatives obtained from β -diketones, like those from ethyl salts of β -ketonic acids, can be transformed into pyridine derivatives. Thus diphenylaceto- α -pyrone yields—

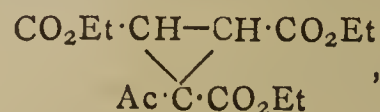


The intermediate product of this reaction, *i.e.*, the ethyl salt, $\text{CO}_2\text{Et}\cdot\text{CH:CPh}\cdot\text{CAc:CPh}(\text{NH}_2)$ (m. p. 161—162°), was isolated.

It was further found that ethylamine, like ammonia, yields, with α -pyrone derivatives, additive compounds with two molecules of the amine. The behaviour of ethyl acetylenedicarboxylate differs from that of ethyl phenylpropionate towards the ethyl salts of benzoylacetic and acetoacetic acids. In these cases, α -pyrone derivatives are not produced, but compounds which are most probably trimethylene derivatives, such as—



a yellow oil with green fluorescence, b. p. 236—237° at 11 m.m., and—



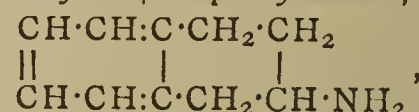
a colourless oil, b. p. 186—187°, at 13 m.m.

97. "Dextro-ac-tetrahydro- β -naphthylamine. By WILLIAM JACKSON POPE.

The only amino-derivative of tetrahydronaphthalene which has previously been resolved into optically active components is ac-1 : 4'-tetrahydronaphthylenediamine; this base was resolved by Bamberger (*Ber.*, 1890, xxiii., 291) by crystallising its acid tartrates.

On adding a solution of half a molecular proportion of ammonium dextro- α -bromocamphorsulphonate to a hot aqueous solution of synthetic ac-tetrahydro- β -naphthylamine hydrochloride, and allowing to cool, a copious separation of *dextro-ac-tetrahydro- β -naphthylamine dextro- α -bromocamphorsulphonate*, $\text{C}_{10}\text{H}_{11}\text{NH}_2\cdot\text{C}_{10}\text{H}_{14}\text{BrOSO}_3\text{H}$, occurs; this salt is very sparingly soluble in water, but crystallises from a mixture of alcohol and acetone in long, colourless needles melting at 185—187°, and in a 5 per cent solution in absolute alcohol has the specific rotation $[\alpha]_D = +78^\circ$.

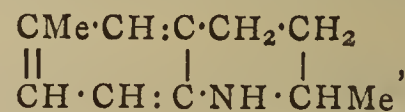
Dextro-ac-tetrahydro- β -naphthylamine,—



is obtained as a colourless oil on treating its dextro-bromocamphorsulphonate with soda, extracting repeatedly with ether, and distilling under reduced pressure. It has the specific rotation $[\alpha]_D = +31^\circ$ at 15° in a 16 per cent solution in benzene. The *dextrocamphorsulphonate*, $\text{C}_{10}\text{H}_{11}\text{NH}_2\cdot\text{C}_{10}\text{H}_{14}\text{OSO}_3\text{H}$, obtained by treating the dextrobase by Reychler's dextrocamphorsulphonic acid, separates from aqueous solutions in large, very lustrous, transparent crystals melting at 215—216°; it has the specific rotation $[\alpha]_D = +43.5$ in a 2 per cent aqueous solution.

98. "The Resolution of Racemic Tetrahydroparatoluquinaldine into its Optically Active Components." By WILLIAM JACKSON POPE and EDMUND MILTON RICH.

The authors have obtained racemic tetrahydroparatoluquinaldine,—



described as an oil by Doebner and Miller (*Ber.*, 1883, xvi., 2464), as a colourless, crystalline substance melting at 32°. It separates in large, transparent crystals from solution in light petroleum, and is almost odourless. The racemic *hydrochloride* crystallises in magnificent prisms melting at 171—173°. Racemic *benzoyltetrahydroparatoluquinaldine*, $\text{C}_{11}\text{H}_{14}\text{NCOPh}$, separates from its solution in acetone in large colourless crystals melting at 103—104°. On adding half a molecular proportion of ammonium dextro- α -bromocamphorsulphonate in aqueous solution to a solution containing one molecular proportion of racemic tetrahydroparatoluquinaldine hydrochloride, *laevotetrahydroparatoluquinaldine dextro- α -bromocamphorsulphonate*, $\text{C}_{11}\text{H}_{15}\text{N}\cdot\text{C}_{10}\text{H}_{14}\text{BrOSO}_3\text{H}$, separates as an oil which soon solidifies; it crystallises from dilute alcohol in colourless needles melting at 195—196°. *Laevotetrahydroparatoluquinaldine*, $\text{C}_{11}\text{H}_{15}\text{N}$, is obtained as a colourless mass on treating its dextromocamphorsulphonate with dilute soda. It separates from its solution in light petroleum in long, colourless, transparent prisms melting at 52—53° having a scarcely perceptible quinoline-like odour; in a 2 per cent solution in benzene at 21°, it has the specific rotation $[\alpha]_D = -80.9^\circ$, and the molecular rotation $[M]_D = -130.2^\circ$. The *hydrochloride* crystallises in magnificent, colourless crystals melting at 192—194°, and in a 2 per cent aqueous solution at 18° has the specific rotation $[\alpha]_D = -68.7^\circ$ and the molecular

rotation $[M]_D = -135.3^\circ$. Benzoyllævotetrahydropara-toluquinaldine, $C_{11}H_{14}NCOPh$, crystallises from alcohol in colourless prisms melting at 100.5° ; in a 2 per cent solution in benzene at 18° , it has the specific rotation $[\alpha]_D = +228.8^\circ$ and the molecular rotation $[M]_D = +606.4^\circ$. Tetrahydroparatoluquinaldine is homologous with the tetrahydroquinaldine recently resolved by Pope and Peachey (*Proc.*, 1899, xv., 124), and the two bases exhibit interesting relationships. Thus dextro- α -bromocamphorsulphonic acid in both cases separates the lævo-base from the externally compensated mixture. Further, in 2 per cent solutions in benzene, the lævo-bases have the same molecular rotation, viz., $[M]_D = -130.20$. Again, on benzoylating the lævorotatory bases, dextrorotatory benzoyl derivatives are obtained, and these have nearly the same molecular rotations in solution in benzene.

99. "Isomeric Salt of Hydrindamine containing Pentavalent Nitrogen." By FREDERIC STANLEY KIPPING, D.Sc., F.R.S.

The base, α -hydrindamine, prepared by reducing the oxime of α -hydrindone (König, *Inaug. Diss. Leipzig*, 1899; Kipping and Revis, *Trans.*, 1897, lxxi., 238), combines with bromocamphorsulphonic acid, yielding unequal quantities of two hydrated salts which can be separated by fractional crystallisation. After having been dried at 100° , the more sparingly soluble salt melts at about 150° , the more readily soluble one at about 130° ; both compounds have the composition $C_9H_{11}N, C_{10}H_{14}BrO \cdot SO_3H$.

Although α -hydrindamine contains an asymmetric carbon atom, and might, therefore, be expected to afford two salts under these conditions, the base regenerated from either of these salts by steam distillation with barium hydrate is optically inactive; the base thus regenerated also gives a hydrochloride and a benzoyl derivative identical in ordinary properties with the corresponding compounds prepared directly from the original externally compensated base. It appears, therefore, that fractional crystallisation of the salt formed with bromocamphorsulphonic acid does not affect a resolution of externally compensated hydrindamine, although this acid has been successfully employed by Pope and Peachey (*Proc.*, 1899, xv., 124) for the separation of the optically isomeric tetrahydroquinaldines.

When, moreover, the base regenerated from one of the isomeric salts is treated with bromocamphorsulphonic acid, it again yields a mixture of the two compounds; the salt of lower melting point is also transformed, partly or entirely, into the isomeride by evaporation with a solution of hydrindamine.

The difference between these two isomerides is not purely crystallographic, since both compounds retain their specific properties on repeated crystallisation from water and other solvents; they have also different specific rotations.

Two different salts, apparently analogous to those just described, are also obtained when hydrindamine is combined with chlorocamphorsulphonic acid, but these two compounds have not yet been studied.

Hydrindamine and lævorotatory *cis*- π -camphanic acid (*Trans.*, 1896, lxix., 943), also combine to form two isomeric anhydrous salts having the composition $C_9H_{11}N, C_{10}H_{14}O_4$; the two compounds can be separated by fractional crystallisation, and though very similar in appearance, they differ in melting point by about 20° , the more sparingly soluble one melting at about 190° , the other at about 170° . The base regenerated from one of these salts appears to be inactive, and the isomerism of the two compounds seems to be of the same kind as that of the two salts of bromocamphorsulphonic acid. The more readily soluble *cis*- π -camphanate can be converted into the isomeride by evaporation with excess of a solution of hydrindamine; the specific rotations of the two salts are apparently different.

As it is impossible at present to arrive at any final conclusion as to the cause of the existence of the various

isomeric salts briefly described in this note, only the more important facts have been recorded. It may be noted also that the assumption, that the isomerism is due to the pentavalent nitrogen atom being in a position in which its free rotation is prevented, explains some of the facts; another possible explanation is, that autoracemation of the free base occurs with great rapidity, but further experimental evidence is required before either view can be accepted.

(To be continued).

SOCIETY OF CHEMICAL INDUSTRY.

GEORGE BEILBY, President.

Annual Meeting, Newcastle, July 12th, 1899.

OUTLINE OF THE PRESIDENT'S ADDRESS.

THE rapid exhaustion of the British coalfields and the serious increase of smoke pollution make it desirable that the questions of fuel and smoke should be treated simultaneously. Our stores of fuel are being recklessly burned up, while the atmosphere, not only of the large cities, but also of the manufacturing districts outside of these, is being increasingly polluted. To place these questions in their true scale and proportion, it is desirable to allocate the total coal consumption of this country under various heads according to the purposes for which the coal is consumed.

The total coal consumed in the United Kingdom in 1898 was 157 million tons, of which—

- 76 million tons were consumed for the production of power for industrial purposes;
- 46 million for the production of heat for industrial purposes;
- 35 million for the production of heat for domestic purposes.

Taking the first two items more in detail, it is estimated that for the production of *power*—

Railways.. ..	consume 10 to 12 million tons.
Coasting steamers..	„ 6 to 8 „ „
Mines	„ 10 to 11 „ „
Factories	„ 38 to 40 „ „

For the production of *heat* for industrial purposes—

Blast furnaces ..	consume 16 to 18 million tons.
Steel and malleable iron works	„ 10 to 12 „ „
Other metallurgical works	„ 1 to 2 „ „
Chemical works, potteries, and glass works	„ 4 to 6 „ „
Gas works	„ 13 to „ „

These figures give a general idea of the magnitude of the problem to be dealt with, and form a sound starting point from which to consider the various remedies which have been suggested. These remedies are broadly divided into two classes.

First.—Improved appliances for the combustion of raw coal, and distribution of the air supply in furnaces.

Second.—The transformation of the raw coal into smokeless fuel by preliminary treatment, either by destructive distillation in gas retorts or in coke ovens, or by its conversion into fuel gas by partial combustion in air and steam.

The distillation of coal in retorts, blast furnaces, and coke ovens was described generally. The amount of each of the crude products obtained from each source was given as below—

Products from the distillation of coal as at present carried on in the United Kingdom.

Gas works distil 13 million tons, and produce—

130,000 million cubic feet of illuminating gas at 650 B.T.U. per cubic foot;
650,000 tons of tar;
129,500 tons of sulphate of ammonia;
7 to 8 million tons of soft coke.

Blast furnaces distil 2 million tons of coal, and produce—

360,000 million cubic feet of fuel gas at 130 B.T.U. per cubic foot;
150,000 tons of tar;
18,000 tons of sulphate of ammonia.

Recovery coke ovens distil $1\frac{1}{2}$ million tons, and produce—

12,500 million cubic feet of illuminating or fuel gas at 600 B.T.U. per cubic foot;
62,000 tons of tar;
900,000 tons of hard coke;
11,000 tons of sulphate of ammonia.

If beehive ovens were entirely replaced by recovery ovens, there would be a further production of—

125,000 million cubic feet of illuminating or fuel gas;
620,000 tons of tar;
9 million tons of hard coke;
110,000 tons of sulphate of ammonia.

Collecting these figures, together, we have from—

	Tar.	Sulphate of ammonia.
Gas works	650,000 tons	130,000 tons.
Shale oil works	— „	37,000 „
Blast furnaces	150,000 „	18,000 „
Recovery ovens	62,000 „	11,000 „
Present totals	862,000 „	196,000 „
After extension of re- covery ovens	620,000 „	110,000 „
Probable totals	1,482,000 „	296,000 „

The effects of the natural development of these industries on the markets for by-products were next considered. It was pointed out that, if any considerable part of the 137 million tons of coal which is at present burned in the raw condition were to be converted into gas—two, coke and ammonia—an altogether new condition of things would arise which would need to be foreseen and provided for. A careful study of the whole subject has led to the conclusion that the natural outlet for the coke and pitch would be found in the manufacture of fuel briquettes, and the President advocated the turning of the very best technical skill to the perfecting of this manufacture. He believed that, with skill and enterprise, it would be possible to make briquettes exactly suited for every purpose from boiler firing to domestic cooking.

The leading types of producer for the making of fuel gas were described, from the original "Siemens" to the most recent "Mond" producer.

Coming to the application of the various remedies, it was pointed out that it was now recognised by engineers that steam boilers could be economically and smokelessly fired either by careful hand stoking or by the modern forms of mechanical stoker. In support of this statement, the report of the Committee on Smoke Preventing Appliances, 1895, was quoted from as follows:—"Finally, the Committee are of opinion that, whilst future experiments and inventions may be the means of introducing new and better methods of treatment in the combustion of fuel, enough is known at present to enable steam users to work their boilers with a fair degree of economy and practically without smoke."

It was pointed out that, if the boilers at present in use, which are badly designed and built, were gradually

weeded out and replaced by properly designed and built boilers, the burning the 57 million tons of raw coal used for steam raising would be accomplished practically smokelessly. Where small power installations were required, it would be better and more economical to replace steam by gas or electric motors. For railways and coasting steamers, an ample supply of smokeless briquettes could be procured by the extension of the coal distillation industries.

For metallurgical and chemical works of all kinds fuel gas is, in the majority of cases, the most suitable fuel, being smokeless and easily controllable. But he thought it unlikely that the average manufacturer would care to add to his capital expenditure as well as to his anxieties by erecting the comparatively costly plant which is necessary for the satisfactory gasification of raw coal. He thought the time was not far distant when centres for the production and distribution of fuel gas would be established in industrial districts. There was nothing to prevent the economical distribution of fuel gas to works within a mile or two of the producing station. If this were accomplished, the conditions of life in industrial localities would be enormously improved, and in time the smoke blots on the face of the country would be wiped out.

Coming to the 35 million tons of raw coal which is burned for domestic purposes, a good deal of attention was given to the present position of domestic gas firing and its relation to heating and ventilation. The desiderata appeared to be warmth, comfort, and ventilation equal to what is obtainable by the use of an open coal fire, and at a cost not more than twice as great. It was pointed out that the gas fire itself had been brought up to a high standard of excellence, but that it generally suffered in efficiency owing to the unsuitability of its setting and surroundings. In this matter the co-operation of the architect and builder with the gas engineer is required, so that house chimneys and flues may be adapted for gas firing.

For domestic heating the fuel briquette, if properly adapted for that particular purpose, might play an important part in the displacement of raw coal and smoky combustion.

Having thus far shown the magnitude of the fuel and smoke questions in the various departments of industry, and also the various remedies which technical skill has placed at our disposal, the President concluded by inquiring briefly into the reasons why these remedies were being so slowly adopted. He suggested that the self-interest of the manufacturer, as well as his public spirit, need to be aroused. He advocated the application of gentle but uniform pressure for the adoption of smokeless methods on consumers of raw coal by a central authority acting under the Government, and instanced the gradual but steady improvement in the character of the emanations from chemical works which had resulted from the judicious administration of the Alkali Acts during the past thirty years.

As a means of bringing all of the different interests which are concerned in this matter into line, it was suggested that the Society might arrange for the holding of a Conference on the subject of Fuel and Smoke, at which the leading technical societies, as well as the actual industries concerned, should be fully represented.

Mixed Anhydrides of Formic Acid.—A. Béhal.—The author has obtained the whole of the series of mixed anhydrides of formic acid. His present paper contains an account of the preparation of formic acetic anhydride and some of its reactions. A study of the latter leads to the conclusion that aceto-formic anhydride reacts on alcohols, giving only the corresponding formic ethers, with formation of acetic acid.—*Comptes Rendus*, cxxviii., No. 24.

NOTICES OF BOOKS.

Sewage Analysis: a Practical Treatise on the Examination of Sewage, and of Effluents from Sewage. By J. A. WANKLYN and W. J. COOPER. London: Kegan Paul, Trench, Trübner, and Co., Limited. 1899. Pp. 220.

IN the introduction the authors draw attention to the great change which has taken place during the now nearly finished century in the disposal of excreta; the convenient method of water carriage has replaced the old-fashioned privy system, but we have now another problem to face, and that is the disposal of the enormous amount of sewage continually being produced. The eight chapters into which about half this volume is divided (the remainder being an appendix dealing with various other matters), deal first with the general analysis of sewage, such as the estimation of specific gravity, chlorine, sulphates, carbonic acid, the ammonia method, &c.; these are all treated in the well known style of one of the authors.

In chapter VI. the authors refer to Sir E. Frankland's combustion process for the estimation of the organic matters in drinking waters. They allege that the process is unsuccessful, and the results impracticable and illusory; but a few lines lower down on the same page they say that as in a typical sewage there would be a 100 m.grms. of organic matter per litre, they can see no insuperable objections to the application of this process to the analysis of sewage.

Now this is not fair to practical chemists; if the authors admit that chemists would be able to measure and estimate 10 parts of organic matter in 100,000 parts of water (as they do), why should they doubt our skill in measuring 0.2 to 0.3 part per 100,000? The difference is not very great, and the smaller amount of gas is much easier to handle.

In the chapter on the utilisation and purification of sewage (No. VIII.) the authors, after reviewing the gradual formation and growth of sewers to our present system as adopted in London, describe their proposed method for the treatment of London sewage. The process is simply that of oxidation, the sewage passing through various tanks so arranged that the ever-changing surface of the sewage shall be exposed to the action of the air for the longest possible time. We see no great objection to it, except that one square mile of tanks would be required.

We are sorry to say that the authors are not friendly to microbes; in fact, a passage in the preface written by one of them would seem to show that he has but a very vague idea as to what they are. He says:—"The wave of fad and fallacy at present passing through the Chemical Society has not disturbed us in our laboratory. Bacteria are interesting creatures, and the study of them is an interesting department of *zoology* and *natural history* (the italics are our own). But bacteria are subject to gravitation and to general physical and chemical action; neither is the burning of the kitchen-fire, nor the action of the steam-engine a manifestation of bacterial action." We never understood that they were.

The book would be greatly improved by the omission of a large amount of *personal* matters which have no interest to the general chemist, and do no good to the authors. There is also evidence of careless proof-reading in many places.

Gutta-percha Trees. ("Les Arbres à Gutta-percha"). By HENRI LECOMTE, Docteur ès Sciences, Professeur au Lycée Saint-Louis, Lauréat de l'Institut. 1 vol., 8vo. 95 pp. Paris: Georges Carré et C. Naud, 3, Rue Racine.

THIS volume will be welcomed by the colonists to whom it is addressed. The possibility of cultivating trees yielding gutta-percha on lands hitherto neglected is henceforth

no longer a matter of doubt. The consequences of successful acclimatisation are correlative with an immense advance in the manufacturing industry, and it is the duty of all interested in the subject to make themselves acquainted with everything which can aid in their undertaking. M. Lecomte's book, drawn up from information obtained on the spot, and addressed to the planters who are always the first interested in any addition to knowledge on their special subject, will be read with advantage by all engaged in the cultivation of exotic plants.

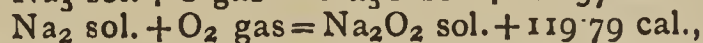
The increasing importance of gutta-percha in European markets renders this work indispensable to electrical engineers, and to the manufacturer desirous of acquiring accurate information on so valuable a commodity.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 24, June 12, 1899.

Heat of Oxidation of Sodium.—M. de Forcrand.—The author recently published the following numbers:—



and has since re-determined the heat of formation of Na_2O . As a mean of several experiments he obtains the number—



Estimation of Hydrogen Phosphide in Mixture of Gases.—J. Riban.—In a recent paper M. Joannis gave an account of the estimation of phosphoretted hydrogen by means of a solution of copper sulphate, this method being used as preferable to that of absorbing the gas by acid cuprous chloride solution, since the cuprous chloride is liable to attack mercury. The author, referring to this paper, states that for many years he has used this latter method with good results, and finds that cuprous chloride in hydrochloric solution does not attack mercury, for it can be kept in burettes over mercury for days without the mercury meniscus being altered. It is the cuprous chloride, partially decomposed owing to contact with air, which attacks the mercury. This should never be used in analysis.

Action of Iodine on Alkalis.—E. Pechard.—When iodine is dissolved in excess of soda or potash, a yellowish solution is produced, with an odour of saffron and possessing oxidising properties. These facts, together with the thermic phenomena produced when these two substances react on one another, lead to the supposition that there exists a hypoiodite analogous to hypochlorite. The author's experiments confirm this supposition, and he also describes a method of estimating the quantity of hypoiodite formed under these conditions. The quantity of hypoiodite formed is almost proportional to the quantity of soda or potash present. The proportion of hypoiodite decreases very rapidly with the temperature, this salt being transformed into iodate as the temperature rises.

Action of Water on Iodomercurate of Ammonia and Iodomercurate of Potassium.—Maurice François.—The decomposition of the iodomercurate, $\text{HgI}_2\text{NH}_4\text{H}_2\text{O}$, by a large quantity of water, produces a precipitate of mercuric iodide and a solution of ammonium iodide. That of the iodomercurate, HgI_2KI , produces a precipitate of mercuric iodide and a solution of potassium iodide. But NH_4I and KI in solution dissolve HgI_2 to a great extent. The solution becomes saturated

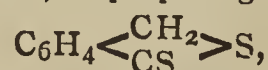
for the temperature of the experiment. This interpretation agrees with observed facts. If the ordinary temperature were 90° , the existence of iodo-mercurates, $\text{HgI}_2 \cdot 2\text{NH}_4\text{I}$ and $\text{HgI}_2 \cdot 2\text{KI}$ would never have been imagined.

Reduction of Copper at a Low Temperature.—Alb. Colson.—Copper, prepared by the reduction of the oxide by hydrogen at a comparatively low temperature (about 200°), possesses several properties which copper prepared at a high temperature does not. It takes fire when in contact with a drop of dry bromine, and retains this property even when cooled to -21° in methyl chloride, or when placed in a vacuum or dry air, but loses the property when in contact with moist air. Copper prepared in this manner does not give the protoxide of nitrogen when acted on with nitric acid. An examination of the density and magnetic properties of this copper show no variation from ordinary copper.

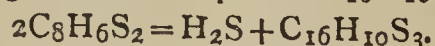
Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxi., November 14, 1898.

Compound of Naphthol and Mercury.—E. Bamberger.—O. Dimroth has lately announced that phenol combines very readily with acetate of mercury; the author noticed the same thing some years ago with β -naphthol, and he described the acetate of β -oxy-naphthyl-mercury, which he obtained by adding an acetic solution of β -naphthol to acetate of mercury. It occurs in the form of bright needles, fusing at 185° with decomposition.

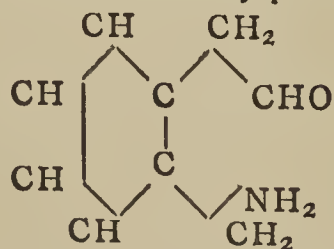
Action of Sulphydrate of Potassium on the Chloride of *o*-Cyanobenzyl.—S. Gabriel and E. Leupold.—A compound, $\text{C}_8\text{H}_7\text{NS}$, can be prepared by reacting with sulphydrate of potassium on the chloride of *o*-cyanobenzyl; but this compound is easily transformed in the presence of an excess of sulphydrate of potassium into $\text{C}_{16}\text{H}_{10}\text{S}_3$, which can also be prepared directly; it is undoubtedly formed according to the equation $2\text{CN}-\text{C}_6\text{H}_4-\text{CH}_2-\text{SH} + \text{H}_2\text{S} = 2\text{NH}_3 + \text{C}_{16}\text{H}_{10}\text{S}_3$; but the mechanism of this decomposition, as well as the constitution of the substance being unknown, the authors undertook to determine them; they arrived at the conclusion that an intermediate product must be formed, and they succeeded, in fact, in preparing dithiophthalide,—



which, when left in alcoholic solution with sulphydrate of potassium, gives the compound $\text{C}_{16}\text{H}_{10}\text{S}_3$.



On the Aminoaldehydes.—E. Maas and R. Wolffenstein.—Tetrahydroisoquinoline is transformed by the action of H_2O_2 into aminomethylphenylacetaldehyde,—



This aldehyde may be benzoylised, but, instead of obtaining by the oxidation of this new derivative a benzoylised acid, it is observed that the benzoyl group is eliminated. The authors have studied the most simple type of the amino-aldehydes with amino-valeraldehyde obtained by the oxidation of piperidine by H_2O_2 . They observed that the benzoylised derivative of this aldehyde eliminated the benzoyl group under the influence of permanganate of potash.

On 3 : 8-Diamidodiphenyl-2 : 9-Dicarboxylic Acid.—C. Bulow and U. von Reden.—Benzidine-*o*-dicarboxylic acid has acquired a certain importance in the arts from the fact that it serves as the primary material for the manufacture of 2 B naphthyl blue. It is prepared

by reducing in alkaline solution the *o*-nitro-benzoic acid, and by transposing the hydrazoic compound which results by boiling with concentrated HCl; 3 : 8 diamido diphenyl-2 : 9 dicarboxylic acid acts by Schotten-Baumann's method with chloride of benzoyl or acetic anhydride, giving the corresponding dibenzoylised or diacetylised derivatives.

Synthesis of some Naphtindulines.—O. Fischer and E. Hepp.—Dinaphtophenylaposafranine is formed by the reaction of HCl nitrosophenyl- α -naphthylamine on phenyl- β -naphthylamine, in the presence of acetic acid on the water-bath. It crystallises in deep violet flakes fusible at 256° or in voluminous needles fusible at 268° . At 130° with alcoholic ammonia this base divides into aniline and rosonaphtindone. (*m.N*)-Ethyldinaphtophenylaposafranine is prepared like the preceding base, by using ethyl- β -naphthylamine. It crystallises in needles with iridescent green reflections, fusible at 255° . Under the influence of concentrated HCl at 210° , it loses $\text{NH}_2\text{C}_6\text{H}_5$, and gives a dinaphthoaposafranine ethyl fusible at 247° . (*m.N*)-ethyl-dinaphthoaposafranine is obtained by treating phenylised safranine with alcoholic ammonia at $120-130^{\circ}$. These salts crystallise well with HCl and HNO_3 .

City and Guilds of London Institute.—Central Technical College.—The Old Students' Association of the College held its Annual Dinner on Thursday, July 6th, at the Restaurant Frascati; the Dean of the College, Professor Armstrong, taking the chair. A large number were present, including the Professors, a number of the Junior Staff, Sir Philip Magnus, Director of the Technological Examination Department, and Mr. A. L. Soper, Assistant Secretary to the Institute. Professor W. E. Ayrton, in proposing the toast of the Association, referred to the progress of the College, and the insufficiency of accommodation due to the continued increase in the number of students; he announced that the Electrical Department would soon be greatly extended by the erection of a large new Dynamo Room nearly six times the size of that at present in use, and occupying a considerable part of the ground floor of the new building of the Royal School of Art Needlework, adjoining the College. The accommodation for this department would be further increased by the completion of a new drawing office and a new lecture theatre. The toast was replied to by Mr. Maurice Solomon, Secretary of the Association. Sir Philip Magnus, in proposing the toast of the College and its Professors, said that when first he had the honour of drawing up the scheme of the College it was prophesied that nobody would go to South Kensington to learn Engineering. But in spite of the fact that they had a harder entrance examination than any other institution of the kind, there were now 250 students in a building only designed for 200. The College was that day entering on a new period in its career, for it was likely to become an integral part of the new University of London, which had decided the day before to move into new quarters at the Imperial Institute, next door to the College. The needs of the College were recognised in the new University by the decision to appoint a faculty of Engineering for the first time in the history of University education, and by the variation of the University Matriculation Examination to suit the requirements of different classes of students. The toast was replied to by Prof. Henrici. The toast of the Athletic Clubs was proposed by Mr. F. S. Miller, who remarked that the prospects of the College Athletics were in a more favourable state owing to the Students' Union having obtained an Athletic ground. Mr. F. C. Hounsfield responded. The toast of the Chairman was proposed by Mr. N. C. Sawers, and Prof. Armstrong in reply alluded to the value of the research work done at the College, especially in relation to the difference between the spirit it introduced and that due to the importance given to text-book information by University Education. A musical programme was supplied by Messrs. Stanger, Mayes, Hounsfield, Trier, Tisdall, Sawers, and Plunket.

THE CHEMICAL NEWS.

Vol. LXXX, No. 2069.

THE ACTION OF HYDROGEN ON SULPHIDE OF SILVER; AND THE INVERSE REACTION.

By H. PELABON.

SULPHIDE of silver can be reduced by hydrogen. This fact was established in 1879 by M. Margottet; he showed that it was sufficient to heat crystallised sulphide of silver for some hours towards 500° in a sealed tube, in an atmosphere of hydrogen, to see that the reduction takes place at various points throughout the mass. The silver set at liberty is in the form of very fine wire similar to filiform native silver.

Inversely sulphydric acid attacks metallic silver.

M. Berthelot (*Am. Chim. Phys.*, Series 5, xvi., p. 440) has verified the fact that sulphuretted hydrogen is decomposed by silver towards 550° with the formation of the metallic sulphide and hydrogen.

We propose studying these two inverse reactions for very wide variations of temperature.

Sealed tubes containing sulphuretted hydrogen and silver, or hydrogen and sulphide of silver, are kept for a sufficiently long time at a definite temperature. At the end of this time they are quickly withdrawn from the furnace, and cooled rapidly by whirling in the air at the end of an iron wire to which they are attached.

The analysis of the gaseous mixture contained in the tubes thus cooled gives the proportion of sulphuretted hydrogen they contain at the temperature of the experiment.

In an experiment in which hydrogen and sulphide of silver were originally present, there is formed, at a temperature of above 250° , sulphuretted hydrogen, the proportion of which in the mixture increases from the first with the time, and then remains steady.

In a tube containing, on the contrary, sulphuretted hydrogen and metallic silver, the proportion of sulphuretted hydrogen diminishes by reason of the formation of sulphide of silver and hydrogen up to a certain limit.

Temperatures above 280° .—For equal temperatures above 280° the two limits are identical. The two reactions in question are limited, and under such conditions of temperature we notice a series of states of equilibrium of the system; silver, sulphide of silver, hydrogen, and sulphuretted hydrogen.

These states can, for example, be characterised by the value of the relation between the partial pressure of the sulphuretted hydrogen in the gaseous mixture and the total pressure of the mixture. Let us call this relationship ρ .

We have said that the value of this relationship diminishes slowly as the temperature increases. In other words, if we represent the successive states of equilibrium of the system by a curve so constructed that the abscissæ are the degrees of temperature, and the ordinates the corresponding values of ρ , the points of this curve should approach the axis of the abscissæ as the temperature increases.

A very simple experiment confirms this view. We prepare two sealed tubes, each divided into two parts by a contraction, in one part we place sulphide of silver, in the other silver; both tubes also contain dry hydrogen gas. The two tubes are heated at the same time in the same furnace, but they are so arranged that the two parts of each tube are at different temperatures, 440° and 350° for example. In one of the tubes it is the sulphide of silver which is at 440° , in the other it is the silver.

The experiment shows that in the first tube the silver remain bright, it is not attacked by the sulphur; in fact, as we have said before, the quantity of sulphuretted hydrogen produced at 440° is but little less than that which should be present in the mixture to attack the silver at 350° . We observe that filiform silver is formed, but it soon ceases to develop.

In the other tube the silver becomes tarnished, and the filiform silver which occurs on the sulphide continues to develop as time proceeds. The quantity of sulphuretted hydrogen produced at 350° is in fact greater than that which should be present in the mixture to attack the silver; this latter destroys a part of this sulphuretted hydrogen forming sulphide, and the hydrogen thus set at liberty reacts again on the sulphide.

The portion of the curve which our experiments have enabled us to trace might be taken for a straight line between 360° and 700° . Between 280° and 360° the points of the curve are situated a little above the straight continuation of the preceding one.

The ordinates of the points of this straight line, of which the abscissæ correspond to the temperatures 360° and 700° , are respectively $\rho = 0.21$, and $\rho = 0.16$.

At 280° we find $\rho =$ about 0.25 . These results are in complete accord with the law of the displacement of equilibrium by variations of temperature, if we admit the following reaction—



a reaction which, at 15° , is accompanied by a disengagement of heat equal to 1.6 calories, and is still exothermic at the temperature of our experiments.

Remarks.—It is not necessary for all parts of the tube to be maintained at the same temperature; the results are absolutely the same if we content ourselves with treating that portion of the tube only which contains the morsel of silver, or sulphide of silver. Equilibrium is reached in such a case in a little longer time, but the limit is characterised by the same value of ρ .

Whatever be the initial conditions equilibrium is reached after heating for a so much longer time as the temperature is lower. While at 580° equilibrium is established in a few minutes, at 440° it requires about forty hours, and at 360° about sixty hours.

At temperatures below 350° both reactions take place with extreme slowness; thus, for example, at 280° it requires about three thousand hours for the sulphuretted hydrogen to cease forming in a tube containing originally sulphide of silver and hydrogen. To increase the speed we introduced into the sealed tubes mixtures of known composition of hydrogen and sulphuretted hydrogen, and we were thus enabled to determine for a given temperature, what mixture remains unchanged in the presence either of silver or of sulphide of silver. It suffices to heat the tubes for ten or fifteen days to notice a change of composition in the systems either too rich or too poor in sulphuretted hydrogen.

On the contrary, at temperatures above 580° , equilibrium is established in a time comparable with the time taken to cool the tubes; from this observation it results that the rapid method of cooling need not necessarily be adopted. It would give much too high figures for the value of ρ . To get over the difficulty we used partly heated tubes of which one end, being outside the furnace, was at a sufficiently low temperature that it could be held in the hand. Equilibrium was established in a similar tube; it was withdrawn quickly from the furnace, and allowed to cool by holding the hot end upwards; the piece of sulphurised silver then fell from the heated part. On contact with the cold glass and cold gas it cools very rapidly; it is then in the presence of a gaseous mixture at a relatively very low temperature, and which can only act on it to a very small degree. But even allowing that a very slight reaction takes place, the amount of sulphuretted hydrogen produced or decomposed would

hardly effect the composition of the gaseous mass in the tube.

By using this method the experiments were only limited, at about 700° , by the softening of the glass.

It may be mentioned that for a known degree of temperature, the limit of the value ρ is independent of the physical state of the silver or of the sulphide of silver. We took pure silver in sheets, in foil, and finely divided, prepared by reducing the chloride in ammoniacal solution by pure zinc. We have used sulphide of silver crystallised and precipitated, either simply dried or dried and melted. All these bodies have, with the same temperature, given us the same value for ρ . This value is still the same if we first put into the sealed tube, quantities of hydrogen, silver, and sulphur insufficient to completely sulphurise the silver.

Remarks on the formation of Filiform Silver.—We have observed that in the reaction of hydrogen on sulphide of silver in sealed tubes, the silver set at liberty only takes the form of filaments when the temperature is below 580° , and consequently at temperatures for which the reduction is not produced too rapidly. At temperatures above 580° , the pieces of sulphide of silver become covered with an almost uniform layer of metallic silver. The most beautiful samples of filiform silver are those obtained by heating crystallised sulphide of silver and hydrogen in a sealed tube to about 400° . At 280° the extremely slow reduction of the sulphide of silver is again accompanied by the production of very fine filaments of silver. In every case filiform silver ceases to be produced when equilibrium is reached. If we take the precaution to place in one part of the tube a certain quantity of lead, so as to continuously decompose the sulphuretted hydrogen formed, the regenerated hydrogen gas will act on a fresh portion of sulphide of silver; under these conditions we note that the silver filaments increase in length as long as there is any undecomposed sulphide of silver remaining. These filaments reach a length of 5 or 6 c.m.; they start at a very limited number of points on the surface of the sulphide, more especially if the latter has been first melted. As a rule their number does not increase; that is to say, the sulphide is only reduced at the point where it is in contact with the extremity of a filament of silver; the metal set at liberty drives before it the filament already formed, and thus the length increases. We have had in the course of our experiments the opportunity of seeing the reduction taking place with five, three, and even one filament of silver.

Temperatures below 280° .—We are able to assert that at the ordinary temperature, when the gas is thoroughly dry, no sulphuration of the silver by sulphuretted hydrogen takes place. Silver is not attacked by sulphuretted hydrogen below a temperature of 180° .

Tubes have been kept for six months at 180° , containing strips of pure silver and known mixtures of hydrogen and sulphuretted hydrogen. The results were the following:—

Composition of the mixture placed in the tube.	Composition of the mixture after two months at 180° .
$\rho = 0.7011$	$\rho = 0.7085$
$\rho = 0.6238$	$\rho = 0.6258$
$\rho = 0.4651$	$\rho = 0.4651$
$\rho = 0.2100$	$\rho = 0.2117$

We see from these figures that the quantity of sulphuretted hydrogen has not diminished.

We have also noticed that sulphide of silver is no longer attacked by hydrogen within these limits of temperature; to observe this we placed in a sealed tube a piece of sulphide of silver, a piece of polished pure copper, and some hydrogen gas. The tube was kept at 180° for one month; the surface of the copper was in no way tarnished. If reduction had taken place, even to a very slight extent, the sulphuretted hydrogen would have formed black sulphide of copper, which would have distinctly changed the appearance of the metal.

To sum up:—1. Below 180° silver is not attacked by

dry sulphuretted hydrogen. Neither is sulphide of silver reduced by hydrogen.

2. Above 280° the two reactions take place with a speed so much the greater as the temperature is higher, but they are limited. The two limits led to the same value of temperature and the same composition of the gaseous system. This composition limit varies very little with the temperature; the gaseous mixture obtained is the richer in sulphuretted hydrogen as the temperature is lower.

3. The silver set at liberty by the reduction of the sulphide is filiform when the operation takes place at a temperature below 580° . At higher temperatures, the silver formed covers the surface of the sulphide uniformly.

There remains to examine what takes place between 180° and 200° : we are at the present time following this up.—*Bull. Soc. Chim.*, Series 3, xxi., No. 9.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JUNE 30TH, 1899.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, July 10th, 1899.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 208 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from June 1st to June 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 208 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during this month shows a still further deficit; rain fell on five days only, the total amount being 1.05 inches. As the average amount for the past thirty years is 2.11 inches, we have a deficit of 1.06 inches, bringing the total deficit for the first six months of the year to 1.75 inches, or 15.8 per cent on the average rainfall.

Our bacteriological examinations of 382 samples have given the results recorded in the following table; we have also examined 48 other samples, from special wells, stand-pipes, &c., making a total of 430 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	408
New River, filtered (mean of 77 samples) ..	20
Thames, unfiltered (mean of 26 samples) ..	1677
Thames water, from the clear water wells of eight Thames-derived supplies (mean of 201 samples)	30
Ditto ditto highest	372
Ditto ditto lowest	0
River Lea, unfiltered (mean of 26 samples) ..	1225
River Lea, from the East London Company's clear water well (mean of 26 samples) ..	19

The bacterial and chemical quality of the Metropolitan waters during June has remained at the same high standard of purity that has characterised it during the last three months. Deficient rainfall may partly account for this improvement, but some of the excellent quality of the water is undoubtedly due to the more efficient regulation of the filtration which is now possible, on account of the large number of bacterial examinations of the Companies' filter wells.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

THE INFLUENCE OF
HYDROCHLORIC ACID IN TITRATIONS BY
SODIUM THIOSULPHATE,
WITH SPECIAL REFERENCE TO
THE ESTIMATION OF SELENIOUS ACID.*

By JOHN T. NORTON, Jun.

IN the method of Norris and Fay (*Am. Chem. Journ.*, xviii., p. 703) for the iodometric determination of selenious acid, advantage is taken of a direct and unique action of sodium thiosulphate upon selenium dioxide in the presence of hydrochloric acid. Most excellent results are claimed for this method; but the explicit statement of the originators of the method, that the amount of hydrochloric acid present does not influence the result, provided the titration is made at the temperature of melting ice, is so extraordinary in view of generally accepted ideas in regard to the interaction of hydrochloric acid and sodium thiosulphate, as to suggest the necessity of careful investigation of this point.

Pickering (*Journ. Chem. Soc.*, xxxvii., p. 135), in his investigation of the reaction between iodine and sodium thiosulphate, has shown that more iodine is required to oxidise the thiosulphate as the proportion of hydrochloric acid increases. He ascribed this effect to the formation of a sulphate, apparently, by the increased activity of the iodine, but the more rational explanation is that, although some sulphate is ultimately formed, the thiosulphate is first partially decomposed into free sulphur and sulphur dioxide. Finkener (*"Anal. Chem.,"* 6 Aufl., p. 620) and Mohr (*"Titrimethode,"* 6 Aufl., p. 279) also mention the decomposing effect of free acid upon sodium thiosulphate.

The sodium thiosulphate used in the following experiments was taken in nearly decinormal solution and was standardised by running it into an approximately decinormal solution of iodine, the value of which had been determined by comparison with decinormal arsenious acid made from carefully re-sublimed arsenious oxide. In the experiments of Table I. the solutions were stirred continuously and kept at a temperature of from 0° to 5° C., while the thiosulphate ran into the acidified liquid. The volume of the solution, though fixed at the beginning as given in the table, was considerably increased during the operation by the melting of the ice. Titrations were conducted as rapidly as possible to avoid the separation of sulphur, which is likely to occur, especially when the acid and thiosulphate are present in large quantities. A perusal of the table shows that the influence of the hydrochloric acid upon the thiosulphate depends chiefly upon the amount of the thiosulphate present and afterwards upon the degree of dilution and its own absolute quantity. Thus when 30 c.m.³ of sodium thiosulphate were employed the effect of 10 c.m.³ of acid is marked at all dilutions within the range of the experiments; the effect of 5 c.m.³ of acid is inappreciable only at a dilution of from

400 to 500 c.m.³, and when 1 c.m.³ of acid is employed the effect is only perceptible at a volume of 100 c.m.³. When 25 c.m.³ of the thiosulphate were used the influence of the acid is less marked; for at a dilution of 500 c.m.³ the effect of 10 c.m.³ of acid is not seen, and 20 c.m.³ of the thiosulphate may be present at any dilution down to 100 c.m.³ in the presence of as much as 10 c.m.³ of the acid, and even considerably more, as experiments not included in the table indicated.

TABLE I.

Volume of liquid at beginning of titration.	Na ₂ S ₂ O ₃ approximately n/10 taken.	Volume of N/10 iodine used in titration.			
		HCl = none.	= 1 c.m. ³ .	= 5 c.m. ³ .	= 10 c.m. ³ .
C.m. ³ .	C.m. ³ .	C.m. ³ .	C.m. ³ .	C.m. ³ .	C.m. ³ .
100	30	30.25	30.75	30.76	31.2
200	30	30.22	30.21	30.56	31.4
300	30	30.20	30.22	31.03	30.9
400	30	30.21	30.20	30.20	30.55
500	30	30.20	30.20	30.21	30.55

Mean = 30.22

100	25	25.29	25.32	25.98	25.70
200	25	25.28	25.34	25.40	25.45
300	25	25.29	25.41	25.38	25.83
400	25	25.27	25.24	25.30	25.63
500	24	25.22	25.23	25.40	25.30

Mean = 25.27

100	20	20.15	20.17	20.33	20.23
200	20	20.20	20.13	20.27	20.23
300	20	20.21	20.15	20.20	20.17
400	20	20.20	20.10	20.27	20.07
500	20	20.10	20.10	20.17	20.13

Mean = 20.15

The slight discrepancies which appear occasionally in the table were due, no doubt, to unavoidable differences in the time of action.

This influence of time upon the reaction between sodium thiosulphate, iodine, and hydrochloric acid comes out clearly in the following series of experiments, in which the thiosulphate was run into the acidified water, cooled to a temperature of from 0° to 5° C. by means of ice, the solution being allowed to stand five, ten, and fifteen minutes. Sulphur was thrown down in nearly every case.

TABLE II.

Volume of the liquid at beginning of titration.	HCl (sp. gr. 1.12) present.	Na ₂ S ₂ O ₃ approximately N/10 taken.	Volume of N/10 iodine used in titration after standing—		
			Five minutes.	Ten minutes.	Fifteen minutes.
C.m. ³ .	C.m. ³ .	C.m. ³ .	C.m. ³ .	C.m. ³ .	C.m. ³ .
200	10	30	30.80	31.30	32.32
200	10	25	25.50	26.00	26.30
200	10	20	20.30	20.70	20.68

The results of the table emphasize sufficiently the necessity of proceeding as rapidly as possible with the titration of sodium thiosulphate by iodine in presence of hydrochloric acid, when the thiosulphate is present in considerable amount. As would be expected, the effect of temperature upon the reaction is also marked. In the following experiments the sodium thiosulphate was run into the acidified water, previously heated to the temperature indicated, and then titrated with iodine.

From these results it is plain that the conditions under which considerable amounts of sodium thiosulphate are titrated in presence of hydrochloric acid must be carefully guarded when accuracy is a consideration. It is also apparent that in all cases the temperature should be reduced as nearly to 0° C. as possible, and rapidity of titration by the iodine is an essential. So long as the

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, Series 4, vol. vii., April, 1899.

TABLE III.

Volume of liquid at beginning of titration.	HCl (sp. gr. 1.12) taken.	Temp. Centigrade.	Na ₂ S ₂ O ₃ approximately N/10 taken.	Volume of N/10 iodine used in titrations at different temperatures.
C.m. ³ .	C.m. ³ .		C.m. ³ .	C.m. ³ .
400	10	6°	25	23.52
400	10	22°	25	23.73
400	10	34°	25	24.35
400	10	42°	25	24.5
400	10	54°	25	25
400	10	64°	25	26.1

thiosulphate present does not exceed 20 c.m.³ of the *n*/10 solution, rapid titration in cold solution proceeds with fair regularity in presence of hydrochloric acid up to 10 c.m.³ of the acid of sp. gr. 1.12. When, however, the amount of thiosulphate is greater than 20 c.m.³ of the *n*/10 solution, care as to the restriction of the acid and dilution of the solution becomes a necessity. Fortunately, in most analytical processes involving the use of the thiosulphate it is possible to add that reagent from the burette to the solution to be acted upon, so that it is destroyed normally as fast as it is introduced, and the danger of interaction with the acid does not occur. In the process of Norris and Fay, however, the method involves the addition of an excess of the thiosulphate to the solution of selenious and hydrochloric acids, and thus the conditions prevail which demand care as to the relation of the acid, the thiosulphate, and the degree of dilution. I have experimented, therefore, with this process under varying conditions.

The process of Norris and Fay for the iodometric determination of selenious acid consists briefly in treating the solution of that acid in ice-water, in the presence of hydrochloric acid, with an excess of a *n*/10 solution of sodium thiosulphate and titrating back the excess of the thiosulphate with iodine. Four molecules of sodium thiosulphate act, apparently, upon one molecule of selenious acid according to a reaction which the authors propose to study.

The selenium dioxide used was made by dissolving presumably pure selenium in nitric acid and evaporating to dryness. The residue was then treated with water, and a little barium hydroxide was added to remove any sulphate which might be present. The solution was then filtered and the filtrate evaporated to dryness. The residue was mixed with four or five times its volume of dried pulverised pyrolusite, and the whole was put into a porcelain crucible and heated. The sublimate of selenium dioxide was carefully collected on a dry watch-glass and put into a drying-bottle as quickly as possible. The pyrolusite prevents any reduction of the selenium dioxide to selenium and the product consisted of beautiful long white needles. This method of preparing the selenium dioxide, which has been used for some time in this laboratory, avoids contamination of the selenium dioxide by nitric acid or water, resulting from the decomposition of the latter, which would be possible in case this reagent were employed in the final sublimation, as is recommended by Norris and Fay. The hydrochloric acid used was of sp. gr. 1.12, as recommended by the originators of the process. For the experiments of Table IV. the dilution at the beginning was fixed at 400 c.m.³, and this was increased in every case by the melting of the ice used to cool the liquid. A glance at the preceding part of this paper will show that at this degree of dilution the hydrochloric acid present has the least effect.

These results, while not so good as those obtained by Norris and Fay, are satisfactory, and show that at this degree of dilution the process is accurate. These results accord closely with those contained in Table I. At a dilution of 400 c.m.³ or in the presence of only 20 c.m.³ of sodium thiosulphate in excess the hydrochloric acid present had no perceptible effect. Of course, it must be kept in mind that the hydrochloric acid acts only upon the excess of thiosulphate which is not taken up by the

TABLE IV.

	Amount SeO ₂ taken.	HCl sp. gr. 1.12 taken.	Volume at beginning of titration.	Excess Na ₂ S ₂ O ₃ employed.	SeO ₂ found.	Error.
	Grm.	C.m. ³ .	C.m. ³ .	C.m. ³ .	Grm.	Grm.
1.	0.0616	10	400	2.28	0.0625	0.0009+
2.	0.0628	10	400	7.11	0.0631	0.0003+
3.	0.0508	10	400	11.4	0.0511	0.0003+
4.	0.0587	10	400	12.8	0.0594	0.0007+
5.	0.0807	10	400	15.3	0.0813	0.0006+
6.	0.0633	10	400	20.85	0.0638	0.0005+
7.	0.0682	25	400	1.11	0.0685	0.0003+
8.	0.0779	25	400	1.35	0.0788	0.0009+
9.	0.0465	25	400	18.93	0.0469	0.0004+
Mean						0.00005+

selenium dioxide. The slight constant plus error in these results cannot be accounted for by errors in the standards; they were all carefully determined. Another preparation of selenium dioxide was made, starting with pure selenium carefully precipitated by sulphurous acid, before putting it through the course of treatment previously described, and the results obtained by the action of the sodium thiosulphate recorded in Table V. agree closely with those of the preceding table.

TABLE V.

	Amount SeO ₂ taken.	HCl sp. gr. 1.12.	H ₂ O at beginning.	Na ₂ S ₂ O ₃ in excess.	SeO ₂ found.	Error.
	Grm.	C.m. ³ .	C.m. ³ .	C.m. ³ .	Grm.	Grm.
1.	0.0562	10	400	9.52	0.0566	0.0004+
2.	0.0651	25	400	11.20	0.0655	0.0004+

The next step was to determine the effect of diminishing the dilution and of varying the strength of acid. The following table gives the results of my experiments.

TABLE VI.

	Amount of SeO ₂ taken.	Volume of H ₂ O at beginning.	HCl (sp. gr. 1.12).	Excess of Na ₂ S ₂ O ₃ .	SeO ₂ taken.	Error.
	Grm.	C.m. ³ .	C.m. ³ .	C.m. ³ .	Grm.	Grm.
1.	0.1042	200	5	24.16	0.1041	0.0001-
2.	0.0611	200	10	13.3	0.0611	0.0000±
3.	0.0850	200	10	21.9	0.0828	0.0022-
4.	0.0757	200	25	13.07	0.0749	0.0008-
5.	0.0540	200	25	21.02	0.0522	0.0018-
6.	0.0674	300	5	10.04	0.0679	0.0005+
7.	0.2416	400	5	15.9	0.2424	0.0008+

It is apparent that at the dilution of 200 c.m.³ we run into difficulties, and the greater the excess of thiosulphate present the greater is the error. When the amount of sodium thiosulphate exceeds 20 c.m.³ a reduction in the amount of acid to 5 c.m.³ is plainly of advantage, as is shown in a comparison of Experiments 1, 3, and 5, and is not disadvantageous at larger dilutions and with smaller amounts of the thiosulphate, as shown in Experiments 6 and 7. The necessity of placing some limits on the method of Norris and Fay has now, I think, been established. The excess of the thiosulphate must be carefully regulated, as well as the temperature. If one has knowledge of the approximate amount of selenious acid in solution, this is not a matter of great difficulty, and things should be so arranged that no more than 20 c.m.³ of the *n*/10 thiosulphate should ever be present in excess of the amount necessary to reduce the selenious acid. If this limit—amounting to 0.0400 c.m. of SeO₂—is placed upon the thiosulphate, so much as 10 c.m.³ of hydrochloric acid (sp. gr. 1.12) may be present without endangering the accuracy of the process, provided the solution is diluted to 400 c.m.³ at the outset; if only 5 c.m.³ of hydrochloric acid are present, the volume at the beginning may be reduced with safety to 200 c.m.³. At all events, 5 c.m.³ of the hydrochloric acid are amply sufficient to bring about the reaction between the thiosulphate and the selenium

at any dilution within the range of my experiments. With these precautions taken, the process of Norris and Fay is simple, rapid, and accurate; without them, as the experimental results indicate, errors of considerable amount may enter.

According to the method of Muthmann and Shafer (*Berichte d. D. Chem. Gesell.*, xxvi., 1008), the determination of selenious acid is effected by the simple addition of potassium iodide to the acidulated solution of selenious acid, and the iodine set free is titrated with sodium thiosulphate. In this procedure the thiosulphate is taken up by the iodine as it is added to the solution, so that the danger of any action between the thiosulphate and the acid is out of the question. It was shown in a former paper from this laboratory (Gooch and Reynolds, *Amer. Journ. Sci.*, 1., 254) that this simple method is inaccurate on account of the incompleteness of reduction in the cold and in presence of the iodine evolved. In a later article, also from this laboratory (Peirce, *Amer. Journ. Sci.*, i., 1896, p. 416), it was shown that selenium may be completely precipitated and determined with accuracy gravimetrically provided the amount of potassium iodide employed is enormously in excess of that theoretically required. This suggests naturally the trial of very large excesses of potassium iodide in the process of Muthmann and Shafer. The details of experiments made in this manner are given in the following table:—

TABLE VII.

SeO ₂ used.	KI.	Volume of	HCl	SeO ₂	Error.
Grm.	Grm.	solution. (sp. gr. 1.12).	C.m. ³ .	found.	Grm.
1. 0.0553	10	150	10	0.0558	0.0005 +
2. 0.0574	5	150	10	0.0567	0.0007 —
3. 0.0683	5	150	10	0.0683	0.0000 ±
4. 0.0487	5	150	10	0.0484	0.0003 —
5. 0.2617	10	150	10	0.2589	0.0028 —

It is obvious that for small quantities of selenium dioxide the accuracy of the process is very much increased by the use of large amounts of iodide, though, of course, the difficulty in reading the end-reaction due to the presence of precipitated red selenium still remains; but the process is still inaccurate when large amounts of selenium dioxide are employed.

In conclusion, I wish to thank Prof. F. A. Gooch for his kind advice and assistance.

THE BLUE PIGMENT IN CORAL (*HELIOPORA CÆRULEA*) AND OTHER ANIMAL ORGANISMS.*

By A. LIVERSIDGE, M.A., LL.D., F.R.S.,
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THE following notes contain the results of some preliminary experiments upon the blue pigment present in the blue coral known as *Heliopora cærulea*. Some fragments of the coral were supplied to me by Professor David, which had been collected by him at Funafuti, when conducting the Coral Reef Exploration Expedition in 1897. He states that the *Heliopora cærulea* is there very abundant in places.

The occurrence of the blue colouring matter in this coral is drawn attention to by the late H. N. Moseley, F.R.S., in the "Challenger Reports,"† who points out that it can be partly separated by dissolving away the calcareous matter by means of hydrochloric acid, and dissolving the pigment in alcohol—he, however, did not

obtain it in a pure form nor did he ascertain its chemical composition: but he gives a full account, illustrated by drawings, of the way in which it occurs in the coral. He states:—"The blue tint is seen in sections of the corallum of *Heliopora cærulea* to be diffused within the hard tissue. The colour is faint or almost absent in the freshly-growing tips of the corallum, and pale in the most recently formed superficial structures generally; it is darkest in the layer lying immediately beneath these, that is to say, in the most recently matured tissue.

"In transverse sections it is seen to be darkest at the surfaces of the walls of the tubes and calicles. In vertical section of the corallum the continuation of the dark blue line marking the margin of the wall of each tube enables the line of the tube to be traced past the superadded tabula, and marks the boundary between the two structures. Very exceptionally, intensely blue streaks are developed more internally on either side of the central canal. The tabulae are almost colourless."

Separation of the Pigment.

On shaking the finely powdered coral with water, the blue pigment does not float, as might have been anticipated, but rather tends to collect at the bottom of the vessel; not sufficiently, however, to be used as a means of separating and collecting it.

As stated by Moseley the readiest way to separate the pigment from the mineral matter of the coral is to dissolve the coral in hydrochloric acid, when the blue colouring matter mixed with animal matter is left in suspension; it can be then filtered off from the calcium chloride solution, which passes through the filter in a colourless condition.

Some of the pieces of coral were old and water-worn, "dead" coral: a specimen of this dissolved in pure hydrochloric acid left a small quantity of insoluble residue amounting to about 0.2 per cent; under the microscope this was seen to consist of rock debris, probably pumice, and a few crystals and groups of crystals of magnetite.

One specimen of such "dead" coral yielded 0.267 per cent of the crude pigment after drying in a water oven. A specimen of the unrolled or "live" coral yielded 1.123 per cent of the dried pigment; the greater yield from the "live" coral appears to be due to the larger amount of animal matter mixed with the pigment.

The crude pigment as set free from the coral by hydrochloric acid is black in colour, and on drying splits up into small pieces with very lustrous conchoidal surfaces, and it is exceedingly tender and so brittle that on crushing much of it flies out of the mortar.

On ignition the pigment gives off nitrogenous odours, intumesces greatly, and the charred residue acquires deep blue, green, and other iridescent colours, similar to those sometimes seen on coke and specimens of hæmatite: this sheen did not readily burn off. No crystalline structure could be detected in the intumesced char—(indigo, if present, would probably have been sublimed and deposited in the cavities, it was accordingly specially searched for)—finally a bulky ferruginous-looking ash was left. The ash was found to contain much phosphoric acid, together with iron, lime, and magnesia.

Moseley states that the blue colouring matter left by hydrochloric acid can be *at once* dissolved off the filter by alcohol; this may be the case with the perfectly fresh coral, but I found that the colour from the old dead coral is only slightly soluble, and even absolute alcohol only dissolves it in part. On evaporation, this extract leaves a dark olive-green residue (indigo leaves a blue residue), which intumesces on ignition and leaves a little ash.

To ascertain its solubility 0.648 gm. of the blue residue left by hydrochloric acid was extracted for some hours with 75 c.c. of absolute alcohol in a percolator over a water-bath; the dark green alcoholic extract when evaporated to dryness in a platinum dish over a water-bath, left a dull dark green liquid coloured and blistered residue weighing 0.115 gm., equal to 17.8 per cent on the crude pigment, and to 0.18 per cent on the original coral,

* Read before the Royal Society of N. S. Wales, December 7, 1898.

† "Zoology," vol. ii., p. 109; see also H. N. Moseley, "On the Colouring Matters of Various Animals, and especially of Deep Sea Forms Dredged by H.M.S. *Challenger*."—*Quart. Journ. of Micro. Soc.*, New Series, January, 1877, vol. xii., p. 2.

On warming, it melts and becomes very fluid, but solidifies on cooling; at higher temperatures it gives off much fume and a disagreeable nitrogenous odour like burnt fish and finally inflames; the carbon burns off very quickly, and some ash is left, viz., the above 0.115 gm. of pigment left 0.0061 gm., or 5.33 per cent. This ash dissolved in hydrochloric acid to a pale yellow colour, and was found to contain iron, phosphoric oxide, lime, and magnesia; the quantity (0.0061 gm.) was insufficient for a complete examination.

Next, 0.648 gm. of the blue colouring matter left by hydrochloric acid was placed in a percolator with 60 c.c. glacial acetic acid, and digested on a water-bath for five or six hours. During extraction in the percolator the original blue colour gradually changed to a dark green.

The extract was evaporated to dryness in a platinum dish over a water-bath, the dried extract weighed 0.171 gm. or 26.45 per cent on the above, or 0.268 per cent on the original coral; hence the acetic acid extracts a larger proportion of matter than alcohol, but the amount of pigment dissolved may not be proportionately greater; the residue was dark green in colour, with a resinous appearance, closely adherent to the dish, without blisters, and somewhat deliquescent.

On heating, the residue melted and assumed purple, blue, and other iridescent tints; it also gave off a disagreeable nitrogenous odour like burnt fish, similar to that from the crude pigment set free by hydrochloric acid and by the alcoholic extract; dense white inflammable fumes were also emitted.

The fixed residue or ash was of a brownish colour, and weighed 0.123 gm., equal to 1.90 per cent. It was found to consist principally of iron, phosphoric oxide, lime, and magnesia. Hence the acetic acid extracts more organic matter, and less ash or mineral matter.

No traces of crystal form could be detected even under the microscope in any of the residues left by the acetic acid solutions.

On evaporating the glacial acetic acid solution of the pigment to dryness over a water-bath and taking up with hot glacial acetic acid a second time, the solution was of a light brown colour instead of blue. The ash from this brown extract also contained iron and phosphoric acid.

When solutions of the coral blue and of indigo in acetic acid are compared side by side, the former is seen to be brighter, and to have a green shade as compared with the indigo blue. The colour is between that of indigo and copper sulphate solution.

When a luminous flame is viewed through it the flame appears of a bluish-green, but when viewed through sulphindigotic acid, or indigo in acetic acid, the flame is more or less reddish-purple.

The spectrum of the coral blue in glacial acetic, formic, and lactic acids, and alcohol, is mainly blue and green, a little of the extreme red is visible and some of the yellow, but the bands are by no means well defined.

Solutions in glacial acetic acid when diluted gradually fade, and a voluminous whitish flocculent precipitate of organic matter is formed, which on ignition burns with a nitrogenous odour.

The undiluted solutions in glacial acetic, in strong formic and propionic acids, faded very slowly, and did not become turbid even after standing six months. The strong solutions of the pigment when exposed to the light do not fade so quickly as those of sulphindigotic acid and of indigo in glacial acetic acid. To test this, solutions of equal depth of colour were made, and left exposed to diffused daylight; the indigo solutions faded and lost the blue tint in a day or two, and after a week or two became practically colourless, while the coral blue solution had faded but slightly. A faded solution of indigo in glacial acetic acid is quite red (salmon colour) by gas-light.

The alcoholic solution fades more quickly than the acetic and formic acid solution, and especially when diluted; a flocculent precipitate is gradually formed, and

the solution turns brown; finally, after two or three weeks, it becomes colourless.

The best solvents for the pigment were found to be formic acid, hot glacial acetic and lactic acids, and absolute alcohol.

The acetic acid solution does not dye wool, silk, or cotton, neither is it fixed by alum or ammonia.

It yields a very pale bluish-lake with alum and ammonia, but the colour fades in a few days. It also yields precipitates with baryta and lime waters, also with lead acetate; these precipitates require further examination.

Action of Reagents.

1. *Alcohols and their Derivatives.*—The crude pigment set free by hydrochloric acid is insoluble in methyl alcohol, also in ordinary alcohol, although soluble in absolute alcohol; it is insoluble in cold amyl alcohol, but on boiling it yields a dull greenish coloured solution. It is also insoluble in amyl acetate. It is insoluble in ether, ethyl acetate, and chloroform; also in acetic anhydride, although glacial acetic acid is one of its best solvents.

When boiled with dichloroacetic acid it yields a pale green solution, with monobromoacetic acid it yields a pale grass-green solution changing to a greenish-brown on boiling.

It is insoluble in oil of winter-green (methyl salicylate).

It is but slightly soluble in aldehyde, in paraldehyde, and in acetone. It is insoluble in glycol; with glycerol it gives a pale greenish solution which quickly fades; it also imparts a pale green colour to hot dichlorhydrin.

2. *Hydrocarbons.*—It is not dissolved by kerosene, naphtha, nor by the pure paraffins, neither is it soluble in such olefines as caprylene and octylene; the latter, however, acquires a slight green tint when heated with the pigment.

With eucalyptus oil it yields a pale green solution, and leaves a greyish gelatinous-looking residue of proteid matter, many times the volume of the original pigment, with black specks of the colouring matter embedded in it.

It does not yield a coloured solution with turpentine, either hot or cold, but after standing in it for some weeks the turpentine lost its original pale straw coloured tint, and became viscid, the pigment also lost its colour, and left a grey residue or skeleton.

3. *Acids.*—With nitric acid the pigment gives a yellow or orange coloured solution fading to yellow, probably due to the formation of picric acid. The colour is not restored by alkalis.

It has already been stated that the pigment is insoluble in hydrochloric acid.

It is insoluble in dilute sulphuric acid, 1 to 4 aq., but with concentrated sulphuric acid it gives a greenish coloured solution in the cold; on boiling the colour darkens, and on filtering through glass-wool an almost black liquid is obtained; on dilution a dusky blue filtrate passes through, but on standing, a black precipitate forms, and the solution becomes colourless; this black precipitate gives a blue solution with acetic acid, so that the pigment is sufficiently stable to resist the action of hot sulphuric acid.

Organic Acids.—Formic acid dissolves it readily both hot and cold to a beautiful blue colour similar to that yielded to acetic acid; on evaporating to dryness over a water-bath it leaves a greenish coloured residue, and this on ignition chars in much the same way as the acetic residue, and leaves a ferruginous-looking ash.

The residue insoluble in acetic acid, and the other above-mentioned solvents after repeated treatment, until the solvent no longer became coloured, is practically black. On heating this residue on platinum it burns slowly without flame, emits a nitrogenous odour, and leaves a considerable amount of ash, which is of a ferruginous colour, and appears to have much the same composition as that from the crude pigment itself.

Propionic Acid.—Slightly soluble in the cold; when

boiled it yields a bright blue solution equal to that in glacial acetic acid, and as permanent.

Propionitril.—Insoluble.

Butyric Acid.—Insoluble in the cold, but yields a pale greenish solution when boiled. *Isobutyric Acid* takes up a little of the blue on warming.

Heptoic, Caprylic, and Nonylic Acids.—Insoluble.

Lactic Acid.—(Ethylidene lactic acid).—Slightly soluble in the cold, but when warmed the solution is a full bright blue, as good as the acetic acid solution. The black residue insoluble in lactic acid imparts no colour to acetic acid. On concentrating the lactic acid solution over the water-bath, the colour gradually fades, and acquires a light brownish tint.

Glycollic Acid.—Gives light green solution, a little darker on warming.

Oleic Acid.—Insoluble, on boiling the acid becomes brown.

Tartaric Acid.—A faint blue colour on boiling.

Oxalic Acid.—Insoluble.

Citric Acid.—Yields a pale blue solution on boiling.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

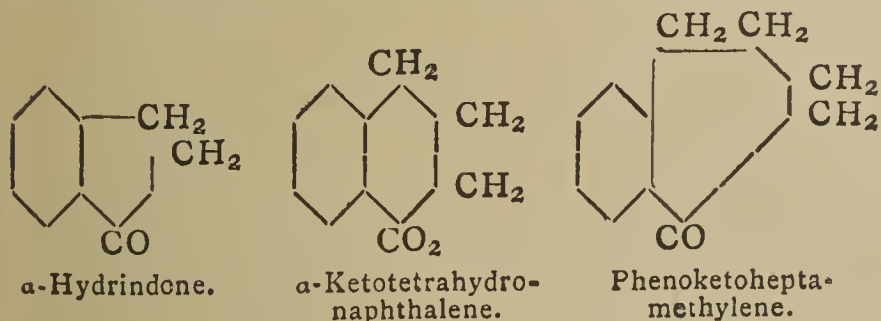
Ordinary Meeting, June 15th, 1899.

Professor T. E. THORPE, F.R.S., President, in the Chair.

(Concluded from p. 18).

100. "Synthesis of Phenoketoheptamethylene." By F. STANLEY KIPPING, D.Sc., F.R.S., and Miss L. HALL.

In continuation of previous work on the formation of cycloid ketones (*Trans.*, 1894, lxx., 480; 1899, lxxv., 144), the authors have studied the action of aluminium chloride on phenylvaleric chloride, $\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COCl}$, and find that, under suitable conditions, the reaction proceeds in accordance with the equation: $\text{Ph}\cdot[\text{CH}_2]_4\cdot\text{COCl} = \text{HCl} + \text{C}_{11}\text{H}_{12}\text{O}$. The product is a ketone, and is in all probability a phenoketoheptamethylene (or phenoheptaphanone) produced by an intramolecular condensation exactly analogous to that which occurs in the formation of α -hydrindone and α -ketotetrahydronaphthalene from the chlorides of phenylpropionic acid and phenylbutyric acid respectively; the relationship between the three cycloid ketones which have now been prepared by this reaction is shown by the following formulæ:—



Phenoketoheptamethylene is a colourless liquid having an odour very like that of peppermint; it is volatile in steam and only very sparingly soluble in water. *Phenoketoheptamethylene semicarbazone*, prepared in the usual manner, crystallises in glistening plates melting at about 219° ; it is decomposed by dilute sulphuric acid, the ketone being regenerated. The analysis of this compound gave C=66.4, H=7.2, the numbers demanded by theory for $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}$ being C=66.4, H=6.9 per cent. As the new ketone contains a closed chain of seven carbon atoms attached to the benzene nucleus, and is the first compound of this kind which has been obtained, the authors are making further experiments to confirm their views as to its constitution, and are also investigating its derivatives.

101. "Organic Compounds containing Silicon." By F. STANLEY KIPPING, D.Sc., F.R.S., and LORENZO L. LLOYD.

Since the publication of various papers by Polis (*Ber.*, 1885, xviii., 1542; 1886, xix., 1012, 1024), very little work has been done on organic compounds containing silicon, more especially as regards those of the aromatic series; the authors, having recently taken up the study of some compounds of this kind, desire to record briefly a few of their results. In the preparation of silicon tetraphenyl by the method described by Polis (*loc. cit.*), a by-product melting at 148° is usually obtained in small quantities; this substance is triphenylsilicol, $(\text{C}_6\text{H}_5)_3\text{Si}\cdot\text{OH}$, and is doubtless identical with the compound obtained by Polis by decomposing triphenylsilicon chloride with water, in spite of the fact that the melting point assigned to it by Polis is only $139-141^\circ$. Triphenylsilicol crystallises in large transparent prisms, and when boiled with acetic chloride it is converted into *triphenylsilicyl acetate*, $(\text{C}_6\text{H}_5)_3\text{Si}\cdot\text{OAc}$; the last-named compound forms colourless prisms and melts at $91-92^\circ$.

When triphenylsilicol is dissolved in glacial acetic acid, and the solution warmed with a little concentrated nitric acid, a colourless, crystalline substance is gradually deposited; this product gave on analysis results agreeing with those required for *triphenylsilicyl ether*, $(\text{C}_6\text{H}_5)_3\text{Si}\cdot\text{O}\cdot\text{Si}(\text{C}_6\text{H}_5)_3$, and as it is also produced by the action of other mineral acids on the alcohol, there is little doubt as to its having this constitution. Triphenylsilicyl ether crystallises from acetic acid in colourless plates and melts at about 221° .

It has also been found that silicon tetrethyl (silicononane) (which was prepared long ago by Friedel and Crafts from silicon tetrachloride and zinc ethyl) can be obtained by treating a mixture of silicon tetrachloride and ethyl bromide with sodium; this method of preparation being a comparatively easy one, the investigation of silicon tetrethyl and its derivatives is also being continued. The estimation of the silicon in many of those silicon compounds which volatilise without decomposition is best carried out by heating in a crucible with concentrated sulphuric acid and weighing the residual silica; although this method may not be so generally applicable as that suggested by Polis (*Ber.*, 1886, xix., 1024), it gives very good results in many cases, and is very easily carried out.

102. "The Velocity of Reaction before complete Equilibrium." By MEYER WILDERMAN, B.Sc., Ph.D.

The reactions investigated were the solidification of supercooled liquids and solutions, the separation of the solid from the pure liquid solvent and from its solutions (*e.g.*, velocity of ice separating from pure water and from solutions of various salts), the separation of dissolved substance from supersaturated solutions, the melting of pure solid solvent in the warmer liquid solvent and in solutions, &c. The reactions take place very quickly, some of them lasting only 15 seconds. Advantage was taken of the fact that the above reactions were accompanied by an evolution or an absorption of heat, which is directly proportional to the amount of ice or salt separated. The velocity of ice separation was determined by the rate of change of temperature in the system. A platinum thermometer was used and the deflections of the galvanometer were photographed on a revolving drum. The author finds that the following general equation holds good for all the above reactions,—

$$\frac{dt}{dz} = C (t_0 - t) (t - t_{ov} + K),$$

where t_0 is the temperature of equilibrium, t_{ov} that at which the reaction is started, K an instability constant. In other words, the velocity of reaction at the time z is directly proportional to the remoteness from the state of equilibrium, to the surface of contact of the two reacting parts of the heterogeneous system, and to the instability constant K . Hence a supercooled liquid or supersaturated solution must spontaneously crystallise when a certain

limit, indicated by K, is passed. From the above equation, it follows that complete equilibrium is "static," whilst incomplete equilibrium is "dynamic."

103. "*The Ultraviolet Absorption Spectra of Albumenoids in relation to that of Tyrosin.*" By A. WYNTER BLYTH.

The author has studied the ultraviolet absorption spectra of egg-albumin, serum, albumin, legumin, casein, Schrotter's albumose, certain toxalbumins, and tyrosin. He comes to the conclusion that the absorption band of ordinary albumin is identical with that of tyrosin. Gelatin, Schrotter's albumose, and certain other albumenoid substances show no band; in these, tyrosin is absent. The author describes a special cell facilitating the study of absorption spectra. A solid block of quartz is cut into steps, the faces of the steps and the back of the quartz being highly polished; the cell is completed by a quartz plate and glass ends; in this way, with one filling, successive thicknesses may be brought before the slit.

104. "*An Explanation of the Laws which Govern Substitution in the case of Benzenoid Compounds.*" (Third Notice). By HENRY E. ARMSTRONG.

This subject was dealt with somewhat fully in two communications made to the Society in 1887 (*Trans.*, li., 258, 583). It was then suggested that the formation mainly of meta-di-derivatives from mono-derivatives containing acidic radicles is perhaps due to the production, in the first instance, of a compound in which the acting molecule is associated with the acidic radicle. The object of the present note is to unreservedly withdraw this hypothesis, and to substitute what is believed to be a rational explanation, which has been arrived at after prolonged study of the subject with the assistance especially of Messrs. Berry and Lewis.

Owing to the readiness with which aniline is acted on by various agents, a false idea has been engendered as to the influence of nitrogen on substitution: in reality, it has a very slight predisposing power. Thus, although azobenzene readily forms an unstable perbromide, it is brominated only with difficulty, and is not easily acted on by substituting agents generally. Diazobenzene perbromide and the diazosulphonate from sulphanilic acid manifest complete indifference to bromine. In point of fact, there is little doubt that the activity of aniline and similar amines is the outcome of the presence of hydrogen in the amino-group; and it is even probable—as suggested in the second of these notices—that the formation of ortho- and para-compounds from primary and secondary amines is always preceded by that of the related compound in which hydrogen in the amino-group is displaced. A similar argument is applicable to the phenols, but there is little direct evidence of any prior displacement of the hydrogen of the hydroxyl group. In any case, in the formation of both ortho- and para-compounds from amines and phenols, there is reason to suppose that nitrogen and oxygen respectively act as attractive and also as orienting elements.

On the other hand, when meta-compounds are formed from amino-derivatives, probably it is because the nitrogen is so situated as to be both destitute of attracting power and possessed of ortho- and para-inhibiting power. Evidence of such inhibiting power is afforded by Miss Evans's observation (*Proc.*, 1895, xi., 235; 1896, xii., 234) that when subjected to the action of bromine, dimethylanilineparasulphonic acid yields a mono-derivative which is stable in presence even of a large excess of bromine at ordinary temperatures—a behaviour altogether different from that of anilineparasulphonic acid, which is at once converted into tribromaniline on merely adding bromine to its aqueous solution.

When negative acid radicles are introduced into the amino-group of aniline, a far greater effect is produced than by positive radicles. Thus, when acetylsulphanilic acid is acted on by a single molecular proportion of bromine, at least 50 per cent of parabromacetanilide is produced, and

the monobrominated acid which is simultaneously formed yields practically nothing but dibromacetanilide when acted on by bromine. The behaviour of benzoysulphanilic acid is similar to that of the acetyl acid.

An equally remarkable effect is produced by alkylating phenolparasulphonic acid. Whereas this acid is converted with extreme facility into the dibromosulphonate, and it is difficult to arrest the action at any earlier stage, the methoxy-, ethoxy-, and benzyloxy-acids prepared from it yield a large proportion of the monobromophenol *ether* together with monobrominated sulphonate when subjected to the action of only a single molecular proportion of bromine, and when further acted on the monobrominated sulphonates yield dibromophenol ethers. But different radicles produce markedly different effects, the benzylated sulphonate giving little besides the bromo-ether, whereas the methylated and ethylated sulphonate yield about equal proportions of bromo-ether and bromo-sulphonate. The corresponding metacresol derivatives behave in a precisely similar way.

Ortho- and para-nitrophenetosulphonates also directly exchange the sulphonic group for bromine, no trace of brominated acid being formed; the corresponding phenol acids yield first a bromonitro-acid, and then the dibromonitrophenol.

But phenyl itself apparently exercises the greatest influence when it takes the places of hydrogen in phenol, phenyl ether para-sulphonic acid, $\text{Ph}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, absorbing but a small proportion of bromine, and without the sulphonic group being displaced.

The difference between an alkylated phenol and phenol is therefore similar to that which obtains between dialkylated aniline and aniline, and at least as great: the introduction of a complex radicle in place of aminic or hydroxylic hydrogen, in fact, produces effects which have not been as yet sufficiently considered.

In order to produce meta-derivatives from amines, it is necessary to paralyse as far as possible the ordinary ortho-para-orienting influence of the amino-group, and to give opportunity for the attack to take place in the nucleus; abundant evidence has been obtained that this can be done in many cases. When acetanilide is acted upon by sulphonating agents, it is initially converted into acetylsulphamic acid, *i.e.*, *sulphamated*; but the sulphamic acid is very prone to undergo change into sulphonic acid, and readily changes into ortho- or para-sulphonic acid, according to the conditions: consequently there is little opportunity for the sulphamic acid to sulphonate, and only traces of meta-acid can be obtained. Sulphamated benzanilide is far more stable, however, and it is easy under appropriate conditions to obtain a large proportion of benzoylmetanilic acid by sulphonating benzanilide; but the action readily proceeds a stage further, the benzoyl also becoming sulphonated. Paracetoluide and orthacetoluide also readily yield acids in which the sulphonic group is meta- to the nitrogen when the conditions are so chosen as to sulphonate the sulphamate which is initially formed. Again, if parabromacetanilide be cautiously dissolved in strongly fuming acid, and the solution be poured on ice and the liquid boiled, a product rich in ortho-acid is obtained; but if the sulphonation be less carefully conducted, so as to give opportunity for all the sulphamate to sulphonate, pure meta-acid is eventually obtained. Both 2:4- and 2:6-dibromacetanilide give meta-acid with far greater facility, the sulphamate in these cases being very insensitive to change, so that the ortho-acid is obtained from the one and the para-acid from the other only by heating the sulphate of the amine at about 180°.

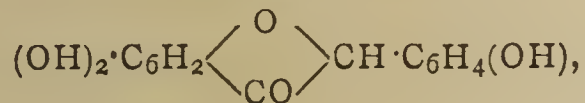
In the case of phenol, although when deprived of the company of hydrogen oxygen requires marked inhibitory powers, being destitute of basic properties, it cannot be rendered sufficiently unattractive to prevent its exercising ortho- and para-orienting power, consequently phenolic compounds do not yield meta-derivatives. But it is very noteworthy that 2:6-dibromophenetol is converted into a

polysulphonic acid with exceptional facility, just as dimethyl- and diethyl-aniline yield, the one a tetra-, the other a penta-derivative when brominated, although aniline yields only tribromaniline.

Briefly stated, the view now advocated is that in compounds which ordinarily furnish meta-di-derivatives, the radicle (NO_2 , CO_2H , &c.), is not only unattractive and possessed of little or no ortho-para-orienting power, but even exercises an inhibiting influence on these positions: consequently, when the two elements of any substituting agent become associated with positions 3 and 4 of the benzene nucleus, separation takes place from 4 rather than from 3, and therefore the meta-derivative is the chief product. The very numerous points of detail which require discussion will be dealt with in a paper in which the results alluded to in the course of this abstract and many others will be fully displayed.

105. "The Colouring Matters of Dyer's Broom and Heather." By A. G. PERKIN and F. G. NEWBURY.

The *Genista tinctoria* (dyer's broom), a yellow dyestuff formerly of some importance, contains two colouring matters, the first identical with the luteolin of weld (*Reseda luteola*), and the second, a new colouring matter, *genistein*. The latter has a composition corresponding to the formula $\text{C}_{14}\text{H}_{10}\text{O}_5$, colourless needles, and yields an acetyl derivative, $\text{C}_{14}\text{H}_7\text{O}_5(\text{C}_2\text{H}_3\text{O})_3$, m. p. $197-201^\circ$, and a tetra-bromo-compound, $\text{C}_{14}\text{H}_6\text{Br}_4\text{O}_5$, colourless needles melting above 290° . On decomposition with alkali, it gives phloroglucinol and an acid of the formula $\text{C}_8\text{H}_8\text{O}_3$, m. p. $147-149^\circ$; this, with fused alkali, forms parahydroxybenzoic acid, and appears to be *parahydroxyphenylacetic acid*. *Genistein dimethylether*, colourless leaflets, m. p. $137-139^\circ$, is insoluble in alkaline solutions, but forms a *monacetyl derivative* of the formula $\text{C}_{14}\text{H}_7\text{O}_3(\text{OCH}_3)_2\cdot\text{Ac}$, fine needles, m. p. $202-204^\circ$. A second product of the methylation, formed in minute quantity, melts at $187-189^\circ$, and appears to be isomeric with the above ether. In dyeing property, *genistein* closely resembles apigenin and vitexin, and to it the constitution of a *trihydroxyphenylketocumaran*,—



has been provisionally assigned. The colouring matter of *Calluna vulgaris* (heather) is quercetin, and there is also present a catechol-tannin in small quantity.

THE ROYAL INSTITUTION.

Sir JAMES CRICHTON-BROWNE, M.D., F.R.S., Treasurer and Vice-President, in the Chair.

At a General Monthly Meeting of the Members of the Royal Institution, held on the 3rd inst., Lord Kinnaird, Mr. A. F. Lindemann, and the Hon. W. J. Ward were elected Members. The Special Thanks of the Members were returned to Mr. Henry Vaughan for his donation of £20, and to Sir Henry Thompson, Bart., for his donation of £25 to the Fund for the Promotion of Experimental Research at Low Temperatures. The cordial thanks of the Members were returned to the Master and Wardens of the Merchant Taylors' Company; to the Lord Mayor and Lady Mayoress; to Dr. and Mrs. Mond; to Dr. and Mrs. Dewar; to Professor William Odling, and to the Teachers of Natural Science at Oxford, for their hospitality to the Members and guests of the Royal Institution during the recent Centenary Celebrations. The Managers reported that they had received gratifying assurances from their guests that the Centenary Celebrations, as a whole, were highly appreciated, and considered not unworthy of the past history of the Royal Institution, and of good augury for that new century of scientific work to which it has

now to apply itself. Thus, Professor Cornu, on his return to Paris, reported to the French Academy of Sciences as follows:—

"La Royal Institution of Great Britain, fondée en 1799, par Benjamin Thompson, Comte de Rumford, fêta les 5, 6 and 7 juin, le Centenaire de sa fondation; S. A. R. le Prince de Galles, Vice-Patron de l'Institution, a gracieusement demandé qu'on lui présentât nos confrères et leur a remis, dans l'une des séances commémoratives, le diplôme de membre honoraire de l'Institution Royale. Lord Rayleigh et M. James Dewar ont rappelé, dans deux remarquables Commemoration Lectures, les principales découvertes faites dans les laboratoires de l'Institution Royale, par Thomas Young, Sir Humphry Davy, Michael Faraday, John Tyndall.

"Les expériences les plus intéressantes ont été exécutées; en particulier, celles qui se rapportent à l'interférence des sons et à l'hydrogène liquide ont excité un véritable enthousiasme. Nous avons pu mesurer ainsi l'immense chemin parcouru depuis un siècle, grâce aux efforts déployés dans cette belle Institution.

"Enfin l'Université d'Oxford a convié tous les savants étrangers présents à Londres à visiter ses collèges, plus de cinq fois séculaires, qui renferment des richesses d'une valeur inestimable.

"Les deux Universités de Cambridge et d'Oxford ont témoigné à nos confrères leur sentiments d'estime et confraternité scientifiques en leur conférant des titres de docteur honoraire.

"Nous rapportons donc de notre séjour parmi les savants anglais non seulement l'impression de la plus cordiale hospitalité, mais encore une véritable admiration pour la manière dont ils cultivent et honorent la science. L'histoire de ces Universités, et particulièrement celle de l'Institution Royale de la Grande-Bretagne, offre un exemple bien instructif: on voit par quelle méthode une nation, jalouse de s'élever au premier rang du progrès scientifique, d'encourager les recherches élevées et d'en faire comprendre les applications, parvient au but qu'elle s'est proposé.

"Elle choisit à chaque époque les savants les plus illustres, leur donne à la fois l'indépendance et les moyens matériels sans lesquels aujourd'hui on ne saurait réaliser de grandes découvertes.

"Il y a là un sujet de méditations et d'études pour ceux qui ont l'honneur de diriger le mouvement scientifique et qui s'efforcent de maintenir notre pays au rang élevé que ses traditions lui imposent."

It is satisfactory to be able to report that the Centenary Celebrations have not affected the pecuniary resources of the Royal Institution, as all expenses in connection therewith have been defrayed by private contributions. A balance remaining over of the sums contributed, amounting to £87, has been paid over to the Fund for the Promotion of Experimental Research.

NOTICES OF BOOKS.

A Treatise on Practical Chemistry and Qualitative Analysis. Adapted for Use in the Laboratories of Colleges and Schools. By FRANK CLOWES, D.Sc. (Lond.). Seventh Edition. Pp. 516. London: J. and A. Churchill. 1899.

BEGINNING simply as a book for teaching practical chemistry to his own class, the author has so increased its scope that it is now offered to the public in the complete and extended form to which it has been gradually brought in the present seventh edition.

The book is divided into seven sections. The first six (omitting the fifth) contain a good practical course for senior students; the fifth is more especially for medical, pharmaceutical, and engineering students, and for those

who, preparing for some definite examination only, wish to become proficient in the analysis of a simple salt.

The seventh section deals with the fitting up and furnishing of laboratories, together with lists of apparatus, reagents, &c., which are required.

The present edition has been thoroughly revised and partly re-arranged and re-paragraphed, in order to facilitate reference. Several illustrations have been added, and important additions to the text have been made in the part dealing with organic chemistry. There is a very complete index of over sixteen pages.

Thirty-fifth Annual Report on Alkali, &c., Works. By THE CHIEF INSPECTOR. Proceedings during the Year 1898. London: Eyre and Spottiswoode. 1899.

As in 1897, we are sorry to see that the work of the inspectors was somewhat interrupted by illness and accident. The number of works now registered under the Acts in England, Ireland, and Wales is 1052. Of these only 86 are works decomposing salt. These numbers show a decrease of one alkali and five others since 1897. There are also 126 works registered in Scotland, of which a separate report is issued. During the year 1898, 4116 visits and 4562 tests were made.

There were, we are pleased to see, only two prosecutions under the Act. In the first, sulphuretted hydrogen was discovered to be escaping to the chimney of the works from the sulphate of ammonia process without any attempt being made to check it by temporary means, those in regular use being unavailable through the stoppage of other plant. The other prosecution was unimportant.

Very few complaints are now received of the escape of hydrochloric acid; the improvement in the plant, together with better technical knowledge, have naturally reduced the escapes of this gas, as well as of chlorine to a very low quantity.

The average escapes of acids of sulphur and nitrogen from exits in sulphuric acid works throughout the country show but little variation from former years.

Dr. Fryer draws attention on page 98 of this report to an improved packing for Glover towers; such results as are given will, if maintained, be of value to other manufacturers.

Very interesting results have been obtained this year in the study of processes for obtaining rectified sulphuric acid of high percentage monohydrate, and are recorded in the report to the Secretary for Scotland, pp. 132-8, on the Kessler process. It is understood that during 1899 a plant will be erected at the Government Works at Waltham Abbey.

To assist proprietors and managers of works scheduled under the Alkali Act, especially the smaller one, the Chief Inspector has, with the object of impressing upon the workpeople employed the responsibilities to which they are subject, suggested that copies of Section 25 of the Act of 1881 should be exposed in prominent positions; the section is here given in full on p. 31.

The individual reports of the different inspectors, giving full details of the work done in their own particular districts, complete the volume.

Practical Methods of Urine Analysis. For Chemists and Druggists. London: *The Chemist and Druggist*. 1899. Pp. 58.

THIS important subject is here dealt with in an able manner, and the information given and methods described are in every respect up to date. It will be found useful to the ordinary medical practitioner, as well as to the pharmaceutical chemist, who is often called upon to make such analyses. The descriptions are clear and the illustrations good.

CORRESPONDENCE.

QUADRIVALENCE OF OXYGEN.

To the Editor of the Chemical News.

SIR,—In a communication recently made to the Chemical Society by J. N. Collie, Ph.D., F.R.S., and Thomas Tickel, relative to the salts of dimethylpyrone, the authors have found it necessary, in order to explain some of their results, to assume the quadrivalence of oxygen. In connection with this matter they point out that J. F. Heyes advocated a similar view (*Phil. Mag.*, 1888) to explain, among other points, the difference between such peroxides as MnO_2 and BaO_2 on the one hand, and CO_2 , SnO_2 , &c., on the other hand; and, further, that Meldola had previously suggested that the oxygen atom in the azo- β -naphthols may be a quadrivalent, but they overlook my own earlier contribution to the subject—which was made to the British Association (Section B) at the Southampton meeting in 1882.

In my paper (see *CHEMICAL NEWS*, September 29, 1882) "On the Activity of Oxygen and Mode of Formation of Peroxide of Hydrogen," I then reviewed the modes of formation of peroxide of hydrogen and ozone, and argued that oxygen exhibits a variable valency, and must in some combinations be viewed as a tetrad.

I am not aware that anyone had previously represented oxygen as a tetrad, and although I am assured and believe that Dr. Collie and his coadjutor did not intentionally neglect a reference to my earlier contribution, I think that the matter is of sufficient importance to place this reclamation on record.—I am, &c.,

C. T. KINGZETT.

Elmstead Knoll, Chislehurst,
July 11, 1899.

CHEMICAL NOTICES FROM FOREIGN SOURCES

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 25, June 19, 1899.

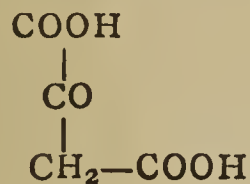
Research on the Vapours emitted by Two Varieties of Mercuric Iodide.—D. Gernez.—It has been known for a long time that mercuric iodide exists in two distinct crystalline forms—one crystallising in the rhombic form, of a red colour and stable at low temperatures; the other orthorhombic, yellow, and stable at high temperatures. The author investigates the conditions under which these two varieties are formed from their vapour. His experiments show that the vapour of mercuric iodide will form under the same conditions of temperature either of the two solid crystalline varieties, according to the nature of the nucleus of crystallisation which is in contact with the vapour.

Decomposition of Carbonic Oxide in presence of Metallic Oxides.—O. Boudouard.—In a previous paper the author has given the results of his researches on the decomposition of carbonic oxide by metallic oxides at temperatures of 445° and 650° . He now continues his researches to 800° . For these experiments the glass vessel used previously has to be replaced by porcelain. From the table of numbers obtained he deduces the result that the reaction of decomposition of carbonic oxide is a function of the time. The quantity of carbonic oxide formed increases in a regular manner, but, as at 650° , the decomposition of carbonic oxide is limited, the experiments show that the reaction stops when the gaseous mixture contains 7 per cent of CO_2 and 93 per cent of CO . It may also be remarked that the velocity of reaction is greater at 800°

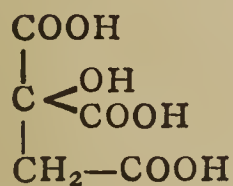
than at 650°. Whilst at 650° it is necessary to heat the tube for six hours to attain the limit, it is enough to heat it for two hours at 800°.

Decomposition of Carbonic Acid in presence of Carbon.—O. Boudouard.—The author has extended his researches on this subject to a temperature of 800°, the conditions of the experiment otherwise being exactly similar to those at the lower temperature. At this temperature the decomposition of carbonic acid is not total, but, as at 650°, the limit which is attained at 800° is the same as that found whilst investigating the decomposition of carbonic oxide (93 per cent of CO and 7 per cent of CO₂). At 925°.—Since the proportion of carbonic acid diminishes more and more in proportion as the temperature is raised, the author substitutes a gravimetric for a volumetric method. He finds that at 925° there still remains in the gaseous mixture resulting from the action of carbonic acid on carbon a proportion of 4 per cent of carbonic acid.

An Inferior Homologue of Citric Acid.—Augustin Durand.—Citric acid has been synthesised by Haller and Held, by acting on prussic acid with acetone dicarbonate of ethylene and transforming the product into citric acid by boiling with strong hydrochloric acid. The author has applied this method to the preparation of the homologues of citric acid by the action of HCN on the acetonic acids. Oxalacetic acid—



is transformed into—



an acid differing from citric acid by CH₂. The calcium salt of this acid crystallises with 5½ molecules of water. The zinc salt is formed as a white powder.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxi., No. 4.

The Condensed Oxides of the Rare Earths.—G. Wyruboff and A. Verneuil.—A very long paper, not suitable for abstraction.

The Complex Salts of Platinum; Oxalates and Nitrates.—M. Vèzes.—Already inserted.

The Symmetrical Dinitrodiphenylcarbamides.—H. Vittenet.—Up to the present only a few substituted diphenylcarbamides were known, such as the metadinitro-, the paradichloro-, and the paradibromo-diphenylcarbamides. The author thought it would be of interest to study and complete the series. For their preparation the general process of reacting on substituted aniline and its homologues was adopted. At the same time the action of the bases on the phenolic carbonates, and particularly on carbonate of phenyl, was also used. In this paper the authors describe successively the nitrocarbamides, the bases derived from them, and their stannic compounds; among these are dinitrodiphenylcarbamide 1:4, diamidodiphenylcarbamide 1:4, dinitrodiphenylcarbamide 1:3, diamidodiphenylcarbamide 1:3, dinitrodiphenylcarbamide 1:2, and diamidodiphenylcarbamide 1:2.

On Essence of Lemon-grass and Essence of Citronel.—J. Flatau.—To decide whether perfectly pure citral would give a mixture of different semicarbazones, the author separated the terpenes which might be present with bisulphite of soda, and after three fractionations, he obtained a pure citral boiling at 119—121° at 22 m.m. The reaction of the semicarbazide with this citral gave crystals melting at from 140° to 155°. It is evidently a mixture of isomeric semicarbazones,

On the Ethers of Essence of Lemon-grass.—H. Labbé.—In a previous paper the author gave an analysis of lemon grass in which he mentioned a residue of 8 or 9 per cent which was not examined. This residue has an agreeable odour like that of the geraniol ethers; it was saponified with 5 per cent alcoholic potash, and in this manner by precipitating with water and washing with ether, an ethereal solution containing terpenic alcohol and an aqueous solution were obtained. This solution, treated with hydrochloric acid, gives a precipitate of fatty acids which, extracted with ether, partially solidify at the ordinary temperature with the exception of a small quantity of oily acids. These acids dissolved in ammonia, and then treated with BaCl₂, give a yellowish white mass of impure salts. In boiling water these partially dissolve. The soluble portion deposits on cooling a white pulverulent mass, which, when dried in vacuo, proved to be a mixture consisting principally of caproic acid. The insoluble part was digested with ether, and decomposed with H₂SO₄. The acids taken up again by ether and converted into a barium salt gave a white powder, which, dried in vacuo, gave the following results:—Ba found, 25.08; the fusing point of the acid was 26—28°; theory requires for caprate of barium (C₁₀H₁₈O₂)₂; Ba = 28.3; the fusing point of capric acid is 31°. To completely identify these two acids the salt was decomposed, and a perfectly white acid obtained, melting at 30.5°. The barium salt prepared from this pure acid gave Ba = 27.9. Thus essence of lemon-grass contains 8 or 9 per cent of capric or caproic ethers of an alcohol which is probably geraniol.

MISCELLANEOUS.

University College of North Wales.—Science Research Scholarship.—The Royal Commissioners for the Exhibition of 1851 have approved the nomination by the University College of North Wales of Mr. Robert Duncombe Abell to a Science Research Scholarship, of the value of £150 a year. Mr. Abell received his early education at Sandbach Grammar School, whence he proceeded in 1892 to the College, with a Cheshire County Council Scholarship, tenable in the Agricultural Department. After completing the two years' course for the College Diploma in Agriculture, he entered upon the B.Sc. course of the University of Wales, which he has just completed, taking first-class honours in chemistry. No honours of this grade have hitherto been awarded to any candidate in the faculty of science. Mr. Abell is about to enter the University of Leipzig, where he proposes to engage in a special research under the direction of Professor Wislicenus.

Leighton Buzzard Water Supply.—Colonel C. H. Luard, R.E., held a public inquiry on the 11th inst., on behalf of the Local Government Board, into an application of the Leighton Buzzard Urban District Council, to borrow £500 for the purpose of providing polarite filters upon the new system so successfully adopted by the Corporation of Hastings, the Southwold Waterworks Company, and other places. The Leighton water being obtained from the lower greensand, contains much iron in solution which requires oxidising and removing, and although the water is otherwise of high organic purity, yet its brown appearance has been a source of inconvenience and great complaint. In order to meet a widespread desire for a clearer drinking supply the Town Council decided to establish an efficient system of filtration, and after lengthened investigation and trials, eventually selected the polarite system of the International Syndicate as the most suitable and economical. The inspector, Colonel Luard, after taking the evidence of Mr. Phelan, the Council's engineer, to the above effect, had the polarite system explained by Mr. Frank Candy, of the International Purification Syndicate, and then proceeded to view the site selected for the filters.

Estimation of the Tartaric Acid in Raw Tartars.—Method adopted by the Chemische Fabrik at Winkelam-Rhein.—For the estimation of total tartaric acid in wine lees and in raw tartars, the following method is recommended:—6 grms. of the finely powdered sample are placed in a 100 c.c. flask, and 9 c.c. of hydrochloric acid diluted to a density of 1.1 are added; this is left for about two hours at the ordinary temperature. The acid extract is then diluted to 100 c.c., well shaken, and filtered through a dry filter. 50 c.c. are then placed in a covered beaker, and 18 c.c. of a solution of carbonate potassium at 20 per cent is added; the whole is then heated until the precipitated carbonate of lime is properly deposited. This precipitate is filtered off, washed with boiling water, and the clear liquid evaporated down to about 15 c.c. in a porcelain crucible. After cooling, 3 c.c. of glacial acetic acid must be added, shake well, and let stand for the night. 100 c.c. of alcohol at 94–96 per cent must then be added while stirring; the precipitated tartaric acid is filtered, washed with alcohol, and finally dissolved in boiling water. The liquid may then be titrated with demi-normal potash. In the case of tartars, or tartrates of lime, 3 grms. of the sample should be taken and digested with 9 c.c. of hydrochloric acid. The solution is made up to 106.5 c.c., and 50 c.c. of this liquid taken for the estimation.—*Zeit. Anal. Chem.*, xxxvii., [5], p. 312.

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THE CHEMICAL NEWS.

VOL. LXXX., No. 2070

NOTE ON THE ELECTRO-DEPOSITION OF BRASS.

By T. J. BAKER and T. J. BAKER, Jun., B.Sc.

WHEN KCN is added to a solution of CuSO_4 in the cold, it is stated that the precipitate first produced is cupric cyanide (Valentin and also Roscoe), but that, on boiling, the precipitate loses $(\text{CN})_2$ and becomes cuprous cyanide.

Both compounds are soluble in KCN solution, and the solution is in common use for copper plating and as a constituent of electro-brassing baths.

It was noticed that the weight of brass deposited from such a solution was frequently much in excess of that of the copper yielded from a copper sulphate solution placed in series with it.

Owing to the evolution of hydrogen during the deposition of the brass, no definite conclusion could be drawn from this observation.

It seemed of interest to examine the matter more carefully, and an apparatus was devised to allow of the collection of the hydrogen.

The cathode consisted of a thin sheet of platinum welded into a cylinder which exactly fitted over a wide glass tube, the latter serving to keep the platinum in shape and to prevent the deposition of brass inside the cathode. The anode was bent into a large cylinder concentric with the cathode. A graduated tube, closed at one end and fitted with a funnel at the other, was filled with solution and then inverted in the depositing vat exactly over the cathode. The volume of the hydrogen thus collected was reduced to 0°C . and 76 c.m., and the weight of cupric copper equivalent to it was calculated.

If c = weight of copper deposited from its cyanide solution,

z = „ zinc deposited from its cyanide solution,

h = „ hydrogen collected,

w = „ copper deposited in the CuSO_4 cell.

Then, if the copper is deposited from its cyanide solution in the *cuprous* condition,—

$$w = \frac{c}{2} + \frac{63.5}{65} z + 31.75 h.$$

In the table, the values of the right-hand member of this equation occupy the 4th column, and the values of w are placed in the 5th column.

I. The first experiments were made with a solution prepared by dissolving the precipitate due to the addition of Na_2CO_3 to 45 grms. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 2 litres of water containing 60 grms. of KCN. This was prepared at a temperature of 13°C ., and when used at that temperature gave the result stated in the first line of the table. When worked at 70°C ., the result given on line 2 was obtained.

II. A zinc solution of the same concentration was then prepared in a similar manner, and at 12°C . yielded the result given on line 3.

III. Mixtures of the copper and zinc cyanide solutions were now made in various ratios, and all were worked at 65 – 70°C . The results were calculated as before, and are contained in the last section of the table.

When it is borne in mind that KCN solution exercises considerable solvent action on copper and zinc, and that each experiment lasted usually about half an hour, the small differences between the numbers in the last two columns are explained.

It may therefore be regarded as certain that the electro-chemical equivalent of copper which is deposited from its cyanide solution, is always that of the metal in its *cuprous* state, and that this is also true when the copper is deposited in combination with zinc as brass.

Weight of deposit from cyanide solution.	Percentage of copper in this deposit.	Volume of hydrogen collected, in c.c.	Weight of cupric copper calculated as CuSO_4 solution equivalent to the total foregoing deposit.	Weight of copper deposited from CuSO_4 solution in series with the cyanide solution.
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Copper Solution.

0.024	100	67.6	0.203	0.197
0.591	100	26	0.369	0.402

Zinc Solution.

0.213	0	43	0.329	0.343
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Brassing Solution.

0.319	84.6	65	0.356	0.397
0.537	83.1	15.3	0.354	0.382
0.474	70.2	10	0.33	0.345
0.316	46.8	24	0.3	0.332
0.369	34.4	15	0.339	0.374

Birmingham Municipal Technical School,
July, 1899.

A SIMPLE METHOD

OF

TITRATING THE AMMONIA IN THE WATERS FROM GAS PURIFIERS.

By M. LUBBERGER.

At most gas-works the ammonia in the waters from the purifiers is estimated by means of a hydrometer; but this method is liable to error, as the presence of ammonia affects the density of the liquid in a very irregular manner. Another method consists in distilling the water from the purifier with lime, and titrating the distillate; but this method is too long.

In the year 1888 Knoblauch proposed a method consisting of adding lime to the liquor, diluted with five times its volume of water. After filtering, the liquor was titrated with normal acid. But in the presence of phenols part of the lime passes into solution, and, under these conditions, the titration gives very irregular results.

The ammonia dissolved in the gas-liquor is principally in the form of sulphide and carbonate. It can therefore be titrated directly with normal acid. The fixed ammonia, on the contrary, requires distilling in the presence of caustic lime, and as the proportion of this fixed ammonia is very small, the author is inclined to admit that the amount is constant for any particular gas-works always working under the same conditions. This hypothesis has been confirmed by a large number of analyses. The author, therefore, proposes to determine the quantity of fixed ammonia in about eight samples, taken at regular intervals spread over several weeks. The average found represents the proportion of fixed ammonia to be added to the results of the daily titrations. For titrating the free ammonia we proceed as follows:—

Three fragments of pure lime, about the size of a nut, are introduced into a flask of 400 c.c. capacity, which is half filled with the liquid to be titrated; the mixture must be shaken, and becomes of a reddish-brown colour. When all the lime is used up, the mixture is cooled, and 50 c.c. filtered off into a graduated flask. The filtered liquor is poured into a beaker, and titrated with demi-normal hydrochloric acid until the colour changes from brown to pale yellow. Of the total acid used we subtract the quantity necessary to saturate the lime in 50 c.c.; the remainder corresponds to the ammonia contained in the

liquor under examination. When operating on 50 c.c., 1 c.c. of demi-normal acid corresponds to 17 grms. of ammonia in 100,000 parts of liquor.

The solubility of the lime in the liquors in question is evidently variable according to the gas-works. It is therefore indispensable to determine it by a certain number of tests, and to take the mean of the results.—*Journ. f. Gasbeleucht.*, 1899, xlii., p. 1.

THE COLORIMETRIC ESTIMATION OF NICKEL.

By MAURICE LUCAS.

For some years past nickel has been used in proportions of from 1 to 3 per cent, to increase the tenacity of extra mild steel; the metal obtained, after tempering and annealing, has a very high limit of elasticity, and is not brittle. These properties have caused it to come into general use, notably in the manufacture of armour plates and of heavy guns, for which it is often used in conjunction with chromium.

For its rapid estimation I made use of the red colouration produced by sulphocarbonate of potassium or sulphocarbonate of ammonium with salts of nickel, a colouration which increases with the proportion of nickel present.

We obtain sulphocarbonate of ammonium by digesting freshly prepared sulphide of ammonium with one-twentieth part of its weight of sulphide of carbon, at a gentle heat for twenty-four hours; the sulphide of carbon is then separated by decantation.

Sulphocarbonate of potassium is prepared, according to Fresenius, by saturating one half of a 5 per cent solution of potash with sulphydric acid, adding the other half, and digesting at a gentle heat with one twenty-fifth of its volume of sulphide of carbon; the deep orange-red solution is separated from the undissolved sulphide of carbon. The deepest coloured of these two reagents is diluted with water so as to give them both the same intensity of colour, and they are then kept in well-stoppered bottles.

When added to a neutral or alkaline solution of a nickel salt they produce a red colouration which fades after a time, above all in the presence of alkaline salts, or on contact with the air.

To obtain these colourations uniform and durable it is necessary to use a large excess of the reagent, and, as this is also coloured red, there would at first sight appear to be some inconvenience.

In reality, however, we do not estimate smaller quantities of nickel than 2 m.grms., and that in a volume of 100 c.c.; we obtain the necessary colouration with 10 c.c. of the reagent, in which the intensity of colour does not correspond to more than one-tenth of a m.grm. of nickel, and as, on the other hand, the typical comparison tubes contain the same proportion, the inconvenience is reduced to simply a slight diminution of sensitiveness; with smaller quantities of nickel we can reduce the proportion of the reagent.

In this manner we make a scale of colourations corresponding to increasing quantities of nickel; each flask contains the same volume of liquid and about the same proportion of ammoniacal salts; care must be taken to keep them from contact with the air by corking them up tightly and using boiled water; the sulphocarbonate is not added until the solutions have been diluted to their proper volumes.

The salts of cobalt give a brown colouration under the same conditions; the process is only applicable after the separation of the two metals nickel and cobalt. This colouration is much more intense with sulphocarbonate of ammonium, which will serve to show the presence of cobalt with the nickel.

Copper gives in equal quantities a colouration almost as strong as that of nickel; we can, with sufficient ac-

curacy, estimate it colorimetrically by means of ferrocyanide of potassium (*Bull. Soc. Chim.*, xix., p. 815), and subtract it from the quantity of Ni+Co found by means of the sulphocarbonate; but it is preferable to separate it first with sulphydric acid.

In the analysis of steels we attack $\frac{1}{2}$ grm. of metal with aqua regia, and make two successive separations by ammonia and an ammoniacal salt. Dilute to 500 c.c., and take three separate quantities of this solution of 50 c.c. each; to the first add 10 c.c. of sulphocarbonate of ammonium; to the second, the same volume of sulphocarbonate of potassium. If the colouration is a deeper brown in the first than in the second, the nickel is mixed with cobalt, and their separation must be effected by any known method; but if not, the first is compared with the scale of coloured tubes, prepared by means of a titrated solution of nitrate of nickel containing 1 decigram. of nickel per litre, taken originally from a much more concentrated solution verified by means of an electrolytic estimation. A salt of ammonia must be added to the comparison tubes.

The third portion of the ammoniacal liquid serves for a second test, profiting by the indications observed in the first case to take advantage of the most favourable conditions.

Finally, on driving off the ammonia, we must make certain that the solution gives no colouration with ferrocyanide of potassium which would indicate the presence of copper; if the latter is present, however, it can be estimated as has been shown above, or, better still, separated with sulphydric acid.

The accuracy of this method is of about one-tenth the proportion of nickel present.—*Bull. Soc. Chim.*, Series 3, xxi., No. 9.

NOTE ON PHOSPHATES.

By M. JULES JOFFRE.

In a previous paper I established the fact that the small coefficients of solubility of apatite and of tricalcic phosphate were not the same in pure water and in water charged with carbonic acid. Although these solubilities are extremely low, the differences observed should, however, have a greater or less influence on vegetation. In fact, as plants absorb and evaporate considerable quantities of water, it is only necessary for a body to be very slightly soluble for it to enter in appreciable quantities into the organism of plant life, and to produce a definite result on vegetation.

I have experimented with the white mustard plant, both in pure sand and in the same sand to which was added peat and carbonate of lime; and again by adding an excess of fertilising elements other than phosphoric acid.

The following are the results I obtained, the means of three successive sets of experiments. They are expressed by taking the weight of the yield without manure at 100, and comparing with this figure the weights obtained with the phosphates experimented on.

Experiments with pure sand:—

Without manure	100
Apatite from Logrosan	100
Tricalcic phosphate (bone-ash) ..	150
Gelatinous tricalcic phosphate ..	246
Monocalcic phosphate	321

Experiments made with a mixture of pure sand, peat, and carbonate of lime:—

Without manure	100
Apatite from Logrosan	112
Tricalcic phosphate (bone-ash) ..	142
Gelatinous tricalcic phosphate ..	197
Monocalcic phosphate	359

As can be seen, apatite (fluophosphate) produces only an uncertain and very slight effect.

The addition of tricalcic phosphate in the state of bone-ash produces, on the contrary, a very marked effect.

We can thus understand that, according as the materials called "phosphates" in commerce, and which are used in agriculture after simply being ground, contain either apatite, or fluophosphate, or tricalcic phosphate, the fertilising power will be very different.

The action of tricalcic phosphate is especially noticeable when it is used in the gelatinous state, that is to say directly after precipitation.

But in spite of the great differences in my results, I do not think we ought to consider these two sorts of tricalcic phosphate as being in different molecular states. The more complete dissemination obtained with the material in the gelatinous state is quite sufficient to explain the larger returns obtained.

Now if we compare all these results with those given by monocalcic phosphate—that is to say, with phosphate soluble in water—we see that there is an enormous difference in its action on vegetation. This phosphate produces results altogether superior, and more especially higher than those obtained with tricalcic phosphate in the gelatinous state, with which we get such excellent dissemination.

We must conclude from this, that it is not only because the monocalcic phosphate is better disseminated that the action is improved, but also because it is in nature absorbed by plants which are able to assimilate it, once it has entered into their organisms. The new experiments I have just made again prove the advantage there is in furnishing plants with phosphates soluble in water.—*Bull. Soc. Chim.*, Series 3, xxi., No. 10.

THE VOLATILISATION OF THE IRON CHLORIDES IN ANALYSIS, AND THE SEPARATION OF THE OXIDES OF IRON AND ALUMINUM.*

By F. A. GOOCH and FRANKE STUART HAVENS.

It is well known that metallic iron is easily acted upon by an excess of chlorine at moderately elevated temperatures with the formation of ferric chloride, and that the product of the action of hydrochloric acid gas upon the metal is ferrous chloride. Out of contact with air, or moisture, both chlorides may be volatilised at appropriate temperatures—the ferric chloride below 200°C .; the ferrous chloride at a bright red heat. If water vapour, or oxygen, or air be present during the heating, both chlorides are partially decomposed with the formation of non-volatile residues, ferric oxide, or ferric oxychloride.

Analytical processes involving the volatilisation of iron at temperatures more or less elevated, in an atmosphere of chlorine or hydrochloric acid, have been the object of considerable attention. Thus Fresenius (*Zeitschr. für Anal. Chem.*, iv., 72), Drown and Shimer (*Journ. Inst. Min. Eng.*, viii., 513), and Watts (*CHEM. NEWS*, xlv., 279) have heated crude iron in chlorine to remove the metal and leave the non-volatile constituents; and Sainte-Claire Deville (*Ann. de Chim. et de Phys.* [iii.], xxxviii., 23) has employed hydrochloric acid to volatilise iron from mixtures of that metal with alumina—obtained by heating the mixed oxides of iron and aluminum in hydrogen according to Rivot (*Ann. de Chim. et de Phys.* [3], xxx., 188)—exposing the mixture, contained in a porcelain boat and placed within a porcelain tube, to the bright red heat of a charcoal furnace—an operation which was bettered by Cooke's (*Amer. Journ. of Science*, [2], xlii., 78) use of

a tube of platinum instead of the porcelain tube and a gas blowpipe in place of the charcoal furnace. Sainte-Claire Deville (*Comptes Rend.*, lii., 1264) showed, further, that ferric oxide may be converted to ferric chloride and volatilised at the heat of the charcoal furnace if the current of hydrochloric acid is sufficiently rapid; but the curious effect was observed that in a sufficiently limited current of the acid no chloride whatever was volatilised, while the amorphous oxide was converted to the highly crystalline oxide of the same composition—a phenomenon which gave rise to a theory of the natural formation of specular iron in volcanic regions.

Quite recently, Moyer (*Journ. Amer. Chem. Soc.*, xviii., 1029) has made record of an unsuccessful attempt (in the course of experimentation upon the volatility of certain chlorides at comparatively low temperatures) to convert ferric oxide completely to ferric chloride by the action of gaseous hydrochloric acid at about 200°C . At this temperature the greater part of the iron sublimed, but a residue remained, which, volatilising neither on long heating at 200° nor upon considerable elevation of the temperature, proved upon examination to be ferrous chloride. In the experiments to be described we have acted with gaseous hydrochloric acid upon ferric oxide made by igniting the nitrate prepared from pure iron deposited electrolytically by high currents passing between electrodes of platinum in a strong solution of ammonio-ferrous sulphate. The oxide, contained in a porcelain boat, was heated within a roomy glass tube over a small combustion furnace. The hydrochloric acid (generated by dropping sulphuric acid into a mixture of strong hydrochloric acid and salt, and dried by calcium chloride) entered one end of the tube and passed out at the other through a water-trap. In early experiments a high-reading thermometer was inserted through the stopper in the exit end of the tube so that its bulb was above and immediately adjacent to the boat carrying the oxide. In this way the actual temperatures of the vapours about the boat were fixed with considerable accuracy; later, after a little experience in gauging the effect of the burners, it was found that the temperatures could be regulated very closely without actually depending upon the thermometer.

We found, as did Moyer, that ferric oxide, submitted to the action of dry hydrochloric acid gas, volatilises partially as ferric chloride at low temperatures— 180° to 200°C .—leaving ultimately a crystalline residue which does not change visibly when heated for an hour or two at 200° , or even at 500° , in the pure dry acid. According to our experience, this residue is generally slightly reddish or salmon-coloured; but sometimes, especially after a second heating, the boat having been withdrawn from the tube or exposed to the atmosphere (and so to moisture), the residue is white. When it is white it dissolves in water, yields the characteristic reaction for a ferrous salt with potassium ferricyanide, gives no reaction with potassium sulphocyanide, and upon treatment in weighed amount with potassium permanganate destroys the amount of that reagent theoretically required for its oxidation upon the supposition that it is ferrous chloride. The slightly coloured residue when treated with water yields a solution showing the reaction of a ferrous salt only, but when treated with hydrochloric acid, and then tested, shows the presence of a trace of iron in the ferric condition. Doubtless the colouration of the residue is due to an included trace of ferric oxide or oxychloride, which after exposure of the containing crystals to slight atmospheric action is more easily reached in the second heating by the gaseous acid. The amount of residue is somewhat variable, but approximates under the conditions of our work to from 5 to 10 per cent of the oxide taken; thus, in one typical experiment 0.1 grm. of ferric oxide left a residue which (withdrawn after cooling) weighed 0.0115 grm.

The greater portion of the ferric oxide volatilises when submitted to the action of the gaseous acid at 200° quickly and abundantly in the form of the greenish vapour of

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, Fourth Series, vol. vii., No. 41, May, 1899.

ferric chloride, and if the operation is interrupted at this stage the residue which remains is nearly black, insoluble in water, slightly soluble in cold hydrochloric acid, and readily soluble in hot hydrochloric acid with the formation of ferric chloride. It is probably something analogous to the oxychloride which Rousseau (*Compt. Rend.*, cxvi., 118), identifies as the product of the action of water upon ferric chloride at 275° to 300° . This dark residue yields to the action of the hydrochloric acid at 180° to 200° only slowly, but ultimately only the residue which is essentially ferrous chloride remains; thereafter little volatilisation occurs within the range of temperature of our experimentation— 200° to 500° .

It is obvious that a reduction of iron in the ferric condition to iron in the ferrous condition takes place under the conditions of our work, and it is difficult to see how this can occur otherwise than by the direct dissociation of ferric chloride under the low partial pressure conditioned by the brisk current of hydrochloric acid gas. The temperature of formation, 180° to 200° , is far below that at which such dissociation is supposed to begin. Thus, Gruenewald and Meyer (*Ber. d. D. Chem. Gesell.*, xxi., 687), found, after cooling, no evidence of the dissociation of ferric chloride which had been heated in the Victor Meyer vapour-density apparatus to 448° in contact or partial mixture with nitrogen; but 10 per cent of the residue obtained by heating to 518° was in the ferrous condition. Friedel and Crafts (*Compt. Rend.*, cvii., 301), however, did see crystals of ferrous chloride at 440° on the walls of a Dumas container filled with the vapour of ferric chloride and nitrogen, the former exerting a partial pressure of 0.75; while ferric chloride volatilised into an atmosphere of chlorine without evidence of dissociation. It seems rather surprising, therefore, to find so large a percentage of dissociation as that shown in our experiments at a temperature so low— 180° to 200° . Curiously, too, we find, on repeating the experiment of heating ferric oxide in gaseous hydrochloric acid, that if the temperature of the oxide is 450° to 500° when the brisk current of acid begins to act, the whole mass of oxide is converted and volatilises without residue. It is hardly to be supposed that the degree of dissociation at 450° to 500° can be less than that at 180° to 200° , and a test of the sublimate, after cooling, shows that it contains a ferrous salt. Plainly, ferrous chloride (formed by dissociation) has volatilised, and inasmuch as the ferrous chloride constituting the residue formed at 180° to 200° does not volatilise in the hydrochloric acid even at 500° , it is plain that the volatility of the former is not determined by the presence of the latter. Apparently, the cause of the completeness of volatilisation must be sought in its rapidity; and this is not an unreasonable hypothesis, if one considers that an action sufficiently rapid to keep above the boat an atmosphere of ferric chloride and its products of partial dissociation, might naturally provide the very condition which would be effective in counteracting the tendency of the residue to dissociate before it volatilises. If this hypothesis is correct, it is plain that the introduction of chlorine gas, the active product of dissociation, into the atmosphere of hydrochloric acid ought to bring about the volatilisation of the residue of ferrous chloride, formed at 180° to 200° , which refuses to volatilise in the acid alone. As a matter of fact, we find by experiment that if a little manganese dioxide is added to the contents of the generator, so that the hydrochloric acid may carry with it a little chlorine, every trace of ferric oxide is volatilised from the boat at 180° to 200° ; and the residue of ferrous chloride found at 180° to 200° when the hydrochloric acid is used alone is likewise volatilised at the same temperature, when the admixture of chlorine is made.

These facts, that ferric oxide is completely volatile in hydrochloric acid gas applied at once at a temperature of 450° to 500° C., and at 180° to 200° if the acid carries a little chlorine, open the way to many analytical separations of iron from substances not volatile under these conditions. In the experiments of the following table we

have applied these methods to the separation of intermixed iron and aluminum oxides. The ferric oxide employed was made, as before, by ignition of the nitrate prepared from iron deposited electrolytically by a strong current passing between platinum electrodes in a solution of ammonio-ferrous sulphate.* The aluminum oxide was made by igniting to a constant weight the carefully washed hydroxide precipitated by ammonia from a pure hydrous chloride thrown down from the solution of a commercially pure chloride by hydrochloric acid (*Am. Journ. Sci.*, ii., 346). The hydrochloric acid gas was made by dropping sulphuric acid into strong hydrochloric acid mixed with salt, and a little manganese dioxide was added when the mixture with chlorine was desired. The experimental details are given in the table.

Fe ₂ O ₃ taken. Grm.	Al ₂ O ₃ taken. Grm.	Al ₂ O ₃ found. Grm.	Error. Grm.	Time. Hours.	Tempera- ture. °C.	Atmo- sphere.
0.1000	—	—	0.0000	$\frac{1}{2}$	450—500	HCl
0.2000	—	—	0.0000	1	"	"
0.1020	0.1015	0.1015	0.0000	$\frac{1}{2}$	"	"
0.2145	0.1006	0.1008	+0.0002	$\frac{3}{4}$	"	"
0.1000	—	—	0.0000	$\frac{3}{4}$	180—200	HCl + Cl ₂
0.1000	0.1032	0.1032	0.0000	$\frac{3}{4}$	"	"
0.1072	0.1013	0.1015	+0.0002	1	"	"
0.2045	0.1032	0.1033	+0.0001	$1\frac{1}{4}$	"	"
0.1050	0.1023	0.1019	-0.0004	$\frac{1}{2}$	450—500	"
0.2008	0.1007	0.1006	-0.0001	$\frac{3}{4}$	"	"
—	0.1087	0.1087	0.0000	1	"	"

The residual alumina tested in several experiments by fusion with sodium carbonate, solution in hydrochloric acid, and addition of potassium sulphocyanide gave no indication of the presence of iron.

The separation of the iron is obviously complete at 450° to 500° when the mixed oxides are submitted at once to the action of hydrochloric acid gas, or at 180° to 200° when chlorine is mixed with the hydrochloric acid. Plainly, the extremely high temperatures employed by Deville are unnecessary if the mixed oxides are submitted at once to the action of hydrochloric acid at 450° to 500° without previous gentle heating in the acid atmosphere. We prefer, however, to use the mixture of chlorine and hydrochloric acid, not only because the temperature of the reaction is lower, but because it needs no regulation, while the danger of error arising from the liability of ferric chloride to dissociate, or from deficiency of oxidation in the oxide treated, or from mechanical loss due to too rapid volatilisation, is avoided.

THE PURIFICATION OF ACETYLENE.

By P. WOLFF.

The average composition of acetylene obtained by means of carbides of Swiss and of American manufacture is as follows:—

	American. Per cent.	Swiss. Per cent.
Acetylene	99.87	99.87
Phosphuretted hydrogen ..	0.04	0.02
Sulphuretted hydrogen ..	0.02	—
Ammonia	0.06	0.04

Carbides of recent manufacture give a gas which contains less sulphuretted hydrogen, and no trace of siliciuretted hydrogen. The quantity of sulphuretted

* The use of an anode of commercially pure iron wire naturally facilitates the operation, but in our experience the deposit thus obtained is likely to carry traces of impurity. In an attempt, too, to prepare pure ferric oxide from the oxalate thrown down out of ferrous sulphate with all precautions, the material obtained still held traces of silica, and possibly alumina, amounting to 0.0004 gm. in 0.1 gm. of the oxide.

hydrogen is always less when the generator contains a large excess of water. A judicious choice of raw materials enables us to reduce the amount of ammonia and phosphoretted hydrogen to a few hundredths per cent; but even such small quantities are still of serious inconvenience.

The method of purification proposed by Frank gives good results; it consists in using acid solutions of certain metallic salts, particularly chloride of copper. A part of the acetylene is transformed into aldehyde.

The author proposes the use of chloride of lime containing a small quantity of an alkaline chromate. The free chlorine is thus absorbed, and the acetylene does not undergo any decomposition.

Frank states that the acid solution of the metallic salt which he uses can be placed in an enamelled vessel, and that the quantity of aldehyde formed is very small. He claims that 1 litre of his solution will purify 14 cubic metres of acetylene, and that it can be regenerated by boiling, followed by aëration—*Fourn. für Gasbeleuchtung*, xli., [42], p. 683.

THE MAXIMUM QUANTITY OF CHLORIDES CONTAINED IN SEA AIR.

By ARMAND GAUTIER.

I HAD occasion to estimate the chlorine in the air out in the open sea; this air was aspirated day and night at the lighthouse at Rochedouvres in the ocean itself, from the 22nd to the 25th October, 1898; the wind was west-north-west, and the weather fine and dry; the air passed slowly by aspiration through a long tube containing glass-wool previously washed and dried, and there deposited any matters that might be in suspension. I caused 341 litres of air at 16° to pass through this plug of glass-wool, under a pressure of 760 to 767 m.m. Carried to my laboratory this glass filter was washed with a little warm water, and the chlorides contained in the filtrate were estimated by means of a decinormal silver solution. A total quantity of 0.00462 grm. of chlorine was found, corresponding to 0.0076 of salt, which by calculation corresponds to 0.022 grm. of chloride of sodium per cubic metre of air.

For an average temperature of 15° this is the maximum; for we may mention that the lighthouse of Rochedouvres, where this air was aspirated, is about 50 or 60 kilometres from the coast, that a good breeze had been blowing for some days from the Atlantic, that half the air was collected during the night, and that although taken at about 9 metres above the level of the sea, it could not contain any of even the smallest particles of spray. This small quantity of salt, 0.022 grm. per litre of air, is thus the maximum. Nevertheless, it suffices perhaps with the traces of iodine which accompany it, to give to sea air the tonic qualities which characterise it.—*Bull. Soc. Chim.*, Series 3, xxi., No. 9.

Some New Diazoic Primary Colouring Materials of the Benzene Series.—C. Bulow and H. Wolfs.—Following their research on the primary diazoic colouring matters, the authors have examined those obtained by reacting with a diazoic compound of the benzene series in acid solution, and then with a diazoic compound of the naphthalene series in alkaline solution, or *vice versa*, on 3:1 oxydimethylaniline. To effect this they used, on the one hand, aniline, *o*- and *p*-toluidine, and *m*-xylydine, and on the other hand, α - and β -naphthylamine. The melting-points and the general appearance of the homologues or isomers of position do not appear to follow any particular rules; but the solution of these materials in sulphuric acid shows characteristic differences. A full account of the preparation and a description of these colouring materials will be found in the original paper.—*Berichte d. Deutsch. Chem. Gesell.*

THE BLUE PIGMENT IN CORAL (*HELIOPORA CÆRULEA*) AND OTHER ANIMAL ORGANISMS.*

By A. LIVERSIDGE, M.A., LL.D., F.R.S.,
Professor of Chemistry in the University of Sydney.

(Concluded from p. 31).

Action of Reagents (continued).

4. *Alkalis*.—In cold dilute ammonia it gives a pale blue solution which gradually fades in the course of a few weeks. It is much more soluble in strong ammonia, also in hot ammonia. On evaporating to dryness the residue is of a brownish colour.

It imparts a greenish colour to potash, both dilute and strong solutions, but when boiled with potash the solution turns brown. Moseley states that the colour is restored by acids, but I did not find this to be the case; a very faint dusky purple only was obtained. When boiled with ammonium, sodium, and potassium carbonates, it in each case yields a dingy slate-coloured solution with a slight purple tinge.

Aromatic Derivatives.—It is insoluble in benzene. Nitrobenzene is coloured green by it, but on heating this darkens and becomes brown. It also imparts a greenish tint to colourless phenol in the cold; on heating it yields a dark solution—the pigment does not, like indigo, appear to be re-deposited on cooling. On evaporating down to dryness over a water-bath and driving off the phenol, the pigment was left as a sap-green resinous-looking film, which under the microscope was seen to be made up of drop-like forms without any trace of crystallisation.

It appears to be insoluble in xylene and also in aniline.

It is partly soluble in cresol (meta) to a dark green solution, and in cold creosote to a pale green; in hot creosote it yields a dark green solution similar to cresol.

The phenol, cresol, xylene, aniline, and other similar solutions were filtered through glass-wool and evaporated, but none of them deposited the pigment in a crystalline form.

Salts.—It was found that the pigment is insoluble in sodium chloride and nitrate, both in the cold and when boiled. The acetate of sodium gave a slight shade of green, and the phosphate a hardly perceptible dusky purple tint. It is also insoluble in magnesium sulphate and stannous chloride. On boiling with stannic chloride, a bright blue solution is apparently obtained, but on filtering, most of the colour is left on the filter, and a very pale blue solution passes through.

Other Reagents.—No colour was imparted to olive oil, and the particles of pigment remained in it unbleached, although exposed to the light for some months, but the olive oil became quite colourless and viscid. It was found to be insoluble also in carbon disulphide, carbon tetrachloride, chloropicrin, thiophen, oil of cloves, cane-sugar solution, &c.

In all cases, although not always specifically stated, the reagent was used hot as well as cold, and in most instances the cold reagent was allowed to stand upon the pigment, with daily shakings for several weeks.

It is bleached by chlorine water (the colour is not restored by alkalis) and a greyish coloured residue is left (several other reagents left a similar residue); this residue or skeleton burns with a nitrogenous odour and leaves a considerable amount of ash—it apparently consists largely of the membrane of the pigment cells and perhaps cornein ($C_{30}H_{44}N_9O_{13}$). The ash is ferruginous in appearance, and contains iron, phosphoric oxide, lime, &c.

A mixture of glucose, ferrous sulphate, and lime does not appear to reduce it, as is the case with indigo.

The colour is discharged by nascent hydrogen (from zinc and hydrochloric acid) also by hydroxyl and sul-

* Read before the Royal Society of N. S. Wales, December 7, 1898.

phurous acid, and it is not restored by neutralising with an alkali.

After the above experiments were completed, the crude pigment was obtained by means of hydrochloric acid from the growing points of "live" coral, *i.e.*, coral which had been gathered while growing.

The tips or growing points were of a dull slaty-blue colour both externally and internally, and I expected them to yield a fuller blue than the "dead" coral, but the pigment obtained was of a pale chlorophyll-green tint, and its solutions in alcohol, glacial acetic and lactic acids were also of a pale green colour; it was practically insoluble in formic acid.

Under the microscope it was seen to be largely made up of membranous matter and cells containing granules of the green pigment. On exposure to light this green pigment gradually darkened somewhat.

Other Animal Blue Pigments.

The late Prof. H. N. Moseley gives an account of certain blue and other animal pigments in his paper on the colouring matter of various animals (*Quarterly Journ. Micro. Science*, xvii., 1877).

Purple Pentacrinin.—He states that many species of pentacrinins readily yield to acidified alcohol colouring matter with well defined spectra. The two principal bands correspond very nearly to those of turacin.

When rendered alkaline by ammonia the solution becomes bluish green. When the acid solution of pentacrinin is carefully concentrated it yields a dark violet amorphous precipitate, which is only slightly soluble in alcohol; it is not soluble in hydrochloric acid alone.

The fresh colouring matter is soluble in fresh water, but remains partly suspended, forming a slightly opaque dark purple solution; on acidifying it entirely dissolves to a beautiful pink; when this is rendered alkaline a green flocculent precipitate is thrown down.

Antedonin.—Antedonins are usually rose, orange, yellow, or brown colour to purple. A dark purple one was dredged off Cape York, Australia. The pigment was insoluble in glycerin, largely soluble in fresh water, and very soluble in weak spirit, and gave an intense fuchsine-coloured solution becoming pinker on dilution with alcohol.

When the alcoholic solution is rendered alkaline by ammonia, it changes to a deep violet, and a flocculent purple precipitate is formed, yielding a violet amorphous powder when dried, insoluble in alcohol and in oil of cloves.

A similar or the same colouring matter was yielded by a holothurian, from the South Indian Ocean; Moseley regarded it as identical with antedonin.

Land Planarians.—Two large species of *Rhynchodemus* were found at Parramatta, N.S.W., one red and the other Prussian blue. The blue is insoluble in alcohol, and becomes red on adding hydrochloric acid and is soluble in acidified alcohol.

Mollusca (*Aplysiopurpurin*).—A purple fluid is emitted by an *Aplysia* abundant on the shore of St. Vincent, Cape Verde; the purple fluid is soluble in alcohol. Said to contain aniline (see "Gmelin," vol. xviii., p. 422).

The purple colouring matter used by the ancients for dyeing linen and woollen, known as punicin, yielded by *Purpura capillus* and other mollusca, is a colourless secretion which becomes purple on exposure to light. It crystallises readily from its solution in aniline and is insoluble in alcohol and ether. Like indigo, it can also be crystallised by sublimation.

Doris.—A *Doris* had the surface of the foot coloured a dark purple; the pigment is soluble in alcohol acidified with hydrochloric acid. The spectrum resembles that from *Aplysia*.

Ianthinin.—The pigment of the purple fluid emitted by *Ianthina* was found to be soluble in spirit to a pale pinkish blue tint, and shows a brilliant red fluorescence, like *æsculin*, which is also blue by transmitted light. On

adding a drop of hydrochloric acid the colour changes to a clear pale blue. The spectrum is well marked. The pigment is also soluble in glycerin, and yields a deep violet-coloured solution. The solution in ether resembles that in alcohol, but leaves a residue which dissolves in absolute alcohol to a blue solution. The ianthinin solutions all faded in a week or two.

Blue Stentorin.—Prof. E. Ray Lankester found that the blue pigment of *Stentor caeruleus* yields two well marked absorption bands in the spectrum, one in the red and the other in the green; also that it is unaffected by dilute acetic, hydrochloric, and sulphuric acids, while dilute potash intensifies it.

He also speaks in the same paper (*Quart. Journ. Micro. Science*, 1873, p. 142; and *Journ. of Anatomy and Physiology*, vol. iv.) of the blue pigment of *Velella* as being probably identical with that of other oceanic hydrozoa; no detached bands are exhibited, but the red and violet ends of the spectrum are cut off.

Fish.—Geo. Francis (Adelaide) describes a bluish green colouring matter from certain species of *Odax* common in St. Vincent's Gulf, S.A., giving a spectrum somewhat resembling that of chlorophyll (for figure and description see *Nature*, Dec. 30, 1875, p. 167). The pigment is soluble in water, rather bluer than chlorophyll; sulphuric acid precipitates it with albumen, but does not destroy the colour; it is bleached by light. The pigment is nitrogenous, and is destroyed by heat, chlorine, acetic acid, alkalis, ammonia, and alcohol.

Turacin (A. H. Church, *Phil. Trans. Roy. Soc.*, 1869, p. 627).—A blue pigment from the feathers of the turaco or plantain-eater; it is soluble in water and contains copper.

Indigo.—Although essentially a vegetable production, it was specially tested for, since an indigo-forming substance occurs in both normal and morbid urine (for authorities see "Gmelin," vol. xviii., p. 407). But no certain indications of the presence of indigo were obtained from the coral pigment.

Pyocyanin.—Formed occasionally in pus. It forms blue acicular crystals arranged in crosses or rosettes. Melts on heating and does not sublime; soluble in water; reddened by acids, but the colour is restored by alkalis. Neither alcoholic nor the aqueous solution is precipitated by alum or lead acetate ("Gmelin," xviii., p. 415).

Hæmocyanin.—This is present in the blood of certain cephalopods, gasteropods, crustacea, and arachnida, and plays the same part as hæmoglobin in the blood of the vertebrates, *i.e.*, as a carrier of oxygen. It enters the gills colourless, absorbs oxygen and becomes blue; in its passage through the tissues it loses oxygen and again becomes colourless. Hæmocyanin contains copper in place of the iron in hæmoglobin. It coagulates at 65° and is precipitated by neutral salts and separated by dialysis (Haliburton, *Journ. Physiol.*, vi., 300).

Emu Egg Shell.—The dark green pigment of this shell gives a beautiful sapphire-blue to glacial acetic acid, also to formic and lactic acids. It is a still more beautiful colour than that from the coral.

Crustacea.—The blue pigment of the lobster and crab becomes red on boiling and by alcohol, but the coral blue does not.

It is unfortunate that so very little is known about the chemical composition of animal pigments, and this is especially the case with the non-crystallisable ones. In these notes I have only drawn attention to such of the animal pigments as appear to be at all allied to the blue coral pigment.

From the foregoing it will be seen that the blue pigment from this coral appears to differ more or less from all of the other animal blues referred to, including the bile pigments, but before it can be definitely stated to be a distinct substance, both this pigment and many of the others require to be further examined.

I am expecting to receive a further supply of the *Heliopora caerulea*, when I hope to be able to obtain the

pigment free from extraneous nitrogenous and other impurities. The pigment (or its accompanying impurities) apparently contains unoxidised sulphur.

THE PHYSIOLOGICAL EFFECT OF CREATIN AND CREATININ, AND THEIR VALUE AS NUTRIENTS.*

By J. W. MALLET, M.D., LL.D.,
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Introduction.

THE nitrogenous extractives, creatin and creatinin, are bodies the physiological importance of which should be determined. Creatin is a normal constituent of flesh, forming about 0.3 per cent of the total nitrogenous material of muscular tissue. It is one of the principal constituents of most meat extracts. The total amount of creatin in the human body may be taken to be something like 90 grms. Creatinin is a normal constituent of human urine. Opinions vary concerning the food value of creatin, creatinin, and other non-proteid amidic bodies. The opinion has often been advanced that such bodies may serve to protect protein, although they cannot serve to build tissue. If they protect protein, it would seem reasonable to suppose that they must yield energy in the body. The general question as to how far the non-proteid amidic substances, which occur most abundantly in foods of animal or vegetable origin, or as the first products of metabolism, are capable of undergoing oxidation in the human body, and thus contributing to the production of energy, is a subject on which more information seemed desirable. The usual methods of determining such bodies are not altogether satisfactory. Therefore, the investigations reported in this Bulletin were made, some studies of the chemical properties of flesh bases and the methods of separating them being necessary before the physiological work could be undertaken.

It has been found necessary to restrict the scope of the inquiry to the so-called flesh bases, creatin and creatinin. An abundant supply of asparagin and a considerable quantity of one or two other amidic compounds of vegetable origin have been procured, but these have not yet been worked with. In the case of asparagin, more has already been done by others in the line of experimenting proposed and less interest attaches to its relations to metabolism in the human body.

Such relations in the case of creatin and creatinin possess a double interest. On the one hand, creatin is a constituent of flesh food, and it is desirable to know whether and to what extent it becomes the material for metabolic change, and thus contributes to the production of energy. On the other hand, the same substance is formed from proteid metabolism in our own muscles, and to a much smaller extent in nervous and other tissues, and it becomes a question of importance what becomes of this creatin, and in what form is it eliminated. There is no reason to believe that creatin or creatinin can be utilised as synthetic material for the building up of the proteid tissues of the body. Creatin is easily changed into its anhydride, creatinin, and this latter substance is found habitually in the urine, so that it might be supposed to represent the slightly changed form in which both the creatin in food and that originating in the living muscles are eliminated. But the quantity of creatinin given off daily in the urine is in general quite small, and, although sufficient as a rule to account for the creatin of the flesh food consumed, the amount seems hardly large enough to cover also the creatin which may be supposed to originate in the living organism in the same time. Hence it has been suggested as probable that in some part of the body

creatin may become converted into other and more complete cleavage products of metabolism, being in large part at least ultimately eliminated as urea. Should we, therefore, consider creatin and creatinin as representing nitrogenous material—received into the living body from without or formed in the body itself—which escapes further metabolism (save the mere conversion of one of these two closely related compounds into the other), and is simply excreted without contributing to the production of energy, or as representing an intermediate stage in the metabolism of protein which on further cleavage does in fact contribute something to the general output of energy of the body.

In connection with this latter hypothesis it may be noted that Stohmann and Langbein* found the molecular heat of combustion of creatin (anhydrous) to be 560 calories,† and that of urea to be 152.2 calories per gram. molecule. Supposing all the nitrogen of creatin to assume the form of urea, and neglecting any thermic result of the formation or oxidation of by-products, as two molecules of creatin will yield three molecules of urea, 331.1 calories will represent the heat evolved for each gram. molecule of the former converted into and eliminated as the latter substance.

Views of Physiologists regarding the Rôle of Creatin and Creatinin.

The divergence and uncertainty of the views held on this subject by leading physiologists are indicated by the following condensed extracts from the works of well-known authorities:—

Thus, H. Newell Martin ("The Human Body," 1881, pp. 433—435) says:—

"In seeking antecedents of urea one naturally turns first to the muscles, which form by far the largest mass of proteid tissues in the body. Analysis shows that they always contain creatin, a body intermediate chemically between proteids and urea. The quantity of this in muscles is practically unaffected by work, and is from 0.2 to 0.4 per cent. Since it is readily soluble and dialysable, and, therefore, fitted to pass rapidly out of the muscles into the blood stream, it is a fair conclusion that a good deal of it is formed in the muscles daily, and carried off from them. Creatin, too, exists in the brain, and probably there and elsewhere in the nervous system is produced by chemical degradation of protoplasm; the spleen also contains a good deal of creatin, and so do many glands. This substance would therefore seem to be constantly produced in considerable quantities by the protoplasmic tissues generally; and since it belongs to a group of nitrogenous compounds which the body is unable to utilise for reconstruction into proteids it must be carried off. The urine, however, contains very little creatin or its immediate derivative, creatinin, and what it does contain depends mainly on the feeding, since it varies with the diet, and vanishes during starvation; so it is probable that this substance is converted into urea and excreted in that form. . . . While the urea resulting from further changes in the creatin formed in the tissues is a measure of the wear and tear of their protoplasm, part of the urea excreted probably has a different source; being due to the oxidation of proteids, as energy liberators or respiratory foods, before they have ever formed a tissue. When plenty of proteid food is taken the urea excretion is largely increased, and that very rapidly, within a couple of hours for example, and before we can well suppose the proteids consumed to have been built up into tissues, and these in turn broken down; in fact, there need be, and

* Quoted in Beilstein's "Handbuch der organischen Chemie," 3rd ed., vol. i., p. 1189. See also article by Stohmann on "The Heat Equivalent of the Nutrients of Food," *Experiment Station Record* 6, p. 598.

† The results of new experiments which Professor Atwater has kindly made with his improved bomb calorimeter on the heat of combustion of both creatin and creatinin furnished by the writer are given further on.

* *Bulletin*, No. 66, United States Department of Agriculture, Office of Experiment Stations.

usually is, under such circumstances, no sign of any special activity of any group of tissues such as one would expect to see if the urea always came from the breaking down of formed histological elements. . . . In artificial pancreatic digestions, when long carried on, two bodies, called leucin and tyrosin, are produced from proteids. It is found that when leucin is given to an animal in its food it reappears in the urine as urea; so the body can convert leucin into that substance. Hence, a possible source of some of the *luxus-consumption* urea is leucin produced during intestinal digestion; and this is very likely turned into urea in the liver. At any rate, the liver, to which the portal vein might carry all leucin thus formed, contains urea, which no other gland does; and when the liver is greatly altered, as in phosphorus poisoning and the disease known as acute yellow atrophy, urea almost entirely disappears from the urine. This latter fact seems to point to a final production of urea in the liver, whatever its immediate antecedents may be; whether muscle creatin, or intestinal leucin, or excess of peptones in the diet."

L. Landois ("A Text-book of Human Physiology," 1891, p. 505), summarises the subject as follows:—

"Although it is surmised that some of the nitrogenous bodies named above, more especially leucin, and perhaps also creatin, are the precursors of urea, yet we can not say definitely how or where the transformation takes place. Perhaps this is effected in the liver, and, it may be, also in the spleen."

The evidence in support of the theory that the liver is the seat of urea production is discussed further on.

Carl von Noorden's ("Lehrbuch der Pathologie des Stoffwechsels," 1893, pp. 70, 71) opinions are in effect as follows:—

"Creatin is undoubtedly a derivative of albumen. It is widely distributed in the body, principally in the muscular system, in which it is contained up to 0.3 per cent (O. Nasse). Creatin rarely comes under consideration as a final product of metabolism, since before its elimination it passes, probably in the kidneys, into its anhydride, creatinin. Only in case of alkaline reaction of the urine can a reverse change, into creatin, occur, in the bladder, or after discharge of the urine.

"The greatest part of the creatinin in the urine comes from the food, since the creatin of the food, easily absorbable from the alimentary canal, passes through the body unchanged, without being oxidised, and is, all of it, discharged as creatinin. He who eats much meat discharges much creatinin; hence it is found more abundantly in the urine of men, adults, and persons in health than in that of women, children, and sick persons; on the other hand, it either occurs in very small quantity or is altogether wanting in the urine of children fed only on milk (free from creatin). The average quantity discharged per day is about 1 grm. for an adult, healthy, and fully fed man; for a woman, 0.65 grm.

"A second portion of the creatinin of the urine comes from creatin which is formed in the body itself, probably in the muscle cells. Only this part is to be regarded as a product of the metabolism of albumen. The muscles contain, as has been mentioned, creatin in abundance; in the urine, apart from the creatin of the food, it occurs only in traces. Whether these traces represent the whole of the creatin metabolism in the muscles, whether in reality the quantity of creatin, as a whole, remains constant, and only these traces are worn off, is unknown. If the change in the stock on hand be a greater one it would have to be supposed that creatin is in the muscle itself converted into urea or other nitrogenous compounds, since leaving the muscle cell as creatin it could only appear unchanged in the urine. . . . Under conditions in which the muscular system of the body is rapidly consumed much creatin is eliminated." (See sections on "Starvation and Fever").

In a very recent treatise William H. Howell ("An American Text-book of Physiology," chapter on "Digestion and Nutrition," 1896, p. 279) says:—

"What becomes of the relatively large quantity of creatin in the muscles? It has been suggested that it is one of the precursors of urea; that it represents an end product of the proteid destroyed in muscle which is subsequently converted to urea in the liver or elsewhere. This supposition is supported by the fact that creatin may be decomposed readily in the laboratory, with the formation of urea among other products. But against this theory we have the important fact that creatin introduced into the blood is not converted into urea, but is eliminated as creatinin."

The subject is discussed at length by M. Foster ("A Text-book of Physiology," 1895, pp. 93, 590—595):—

"Urea does not arise in muscular substance itself as one of the immediate waste products of muscular substance.

"There is, however, always present in relatively considerable amount, on an average about 0.25 per cent of wet muscle, a remarkable body, *creatin*. This is in one sense a compound of urea: it may be split up into urea and sarcosin. This latter body is a methyl glycin; that is to say, a glycin in which methyl has been substituted for hydrogen, and glycin itself is amido-acetic acid, a compound of amidogen; that is, a representative of ammonia and acetic acid. Hence creatin contains urea, which has close relations with ammonia, together with another representative of ammonia, and a surplus of carbon and hydrogen arranged as a body belonging to the fatty acid series. . . . In dealing with the chemistry of muscle we saw that urea was conspicuous by its absence from the extract of muscle, whereas a very appreciable quantity of creatin was invariably present, and indeed was the prominent nitrogenous crystalline constituent of that extract. It seems difficult to resist the conclusion that creatin is the main normal nitrogenous product of the metabolism of skeletal muscles. If we accept this view, then upon the fact of the presence of creatin in, and the absence of urea from, the muscle itself, we may base the conclusion that while the muscle produces creatin as an antecedent of urea, the creatin so produced is converted into urea in some part of the body other than the muscle itself. . . . We must not, however, leave this statement without referring to a difficulty. Creatinin, as we have seen, is so frequently found in urine as to be regarded as a normal constituent, at all events of human urine; and creatinin is, as we have seen, the urinary form, so to speak, of creatin; the one body easily changes into the other by the assumption or removal of H_2O . This suggests the question: Is not the creatinin of urine the representative of the creatin of the muscles, which is thus excreted directly without undergoing the change into urea just discussed? In answer to this we may say in the first place that the quantity of creatinin in urine, though variable, is small; we may put the average at about 1 grm. in twenty-four hours. Now, muscle contains from 0.2 to 0.4 per cent of creatin; and this, taking the total muscle of the body (to say nothing of other sources of creatin which we shall mention presently) at about 30 kilos., would give 60 to 120 grms. creatin as present in the muscles of the body at any one moment. We can hardly suppose that the metabolism of muscle is so slow as out of this stock only to provide the 1 grm. of creatinin in twenty-four hours. Moreover, the creatinin in urine vanishes during starvation, is very markedly increased by a diet of flesh which contains creatin, and is not increased either by muscular exercise (which, however, would only indirectly affect the nitrogenous metabolism of muscle) or by such conditions—fever, for instance—as notably increase the urea of urine by increasing the nitrogenous metabolism of muscle. We infer, therefore, that the normal presence of creatinin in urine is due to the direct administration of creatin present in a (normal) flesh diet, and has nothing to do

with the muscular metabolism of the individual who is secreting the creatinin in his urine.

"The fact, however, that the creatin present in the muscle of the food and absorbed from the alimentary canal does not undergo a change into urea, but is excreted as creatinin—that is, virtually as creatin—warns us to be careful in adopting the conclusion arrived at above, that the creatin produced by muscular metabolism in the living body is a conspicuous antecedent of the urea of the urine. It is difficult to see why creatin passing into the blood of the capillaries of the muscle should be changed into urea, while that which passes into the capillaries of the portal system is not; for reasons which will be apparent presently we should rather expect that the latter, being more directly exposed to the influence of the liver, would be more readily and more completely converted than the former. Indeed, the question forces itself upon us: Is creatin, after all, the natural main product of the nitrogenous metabolism of muscle? Is it possible that in the normal metabolism of the living muscle the nitrogen leaves the muscular substance, and passes into the blood in another form, as some substance not creatin, and that it is as the muscle dies that creatin is formed, just as the solid myosin is unknown to the living fibre, but makes its appearance in a dying one? We have no positive evidence, however, that this is so, and meanwhile may continue to suppose that creatin is formed, and that in consequence creatin is a conspicuous antecedent of the urea of the urine; but we must not regard this as proved. . . . we may probably consider the metabolism of the nervous system as a mere addition to that of the muscular system, at least as regards the point on which we are now dwelling. The amount of nitrogenous metabolism taking place in connective tissue, cartilage, bone, and the skin is probably still less. . . . The nitrogenous metabolism of the glands, however, more particularly that of the liver, does deserve special consideration. . . . we have seen that pancreatic juice may carry part of the proteids on which it acts beyond the stage of albumose and peptone, and reduce that part into leucin, tyrosin, and other bodies. . . . We have seen reason to think that proteids of a meal are absorbed, not by the lacteals, but by the portal blood vessels, and such bodies as leucin probably take the same course. This being so, all these bodies pass through the liver and are subjected to such influences as may be exerted by the hepatic cells. . . . we have, however, a convergence of evidence that the last stage of the process, namely the conversion into urea of some or other product of proteid metabolism which although allied to is not exactly urea, does occur in the liver. In the first place, a large quantity of urea seems to be present in the liver of mammals; in this respect the liver presents a strong contrast to the muscles. . . . In the second place, in certain cases of a form of disease of the liver known as acute yellow atrophy, in which the hepatic cells are so changed that their functional activity is largely diminished, the urea of the urine not only undergoes a very marked decrease, but appears to be replaced to a very large extent by leucin. This fact suggests that leucin (and not, for instance, creatin) is the chief immediate product of the nitrogenous metabolism of the body, and that the leucin thus produced is, in a normal state of things, converted into urea by the liver."

Previous Researches upon the Nutritive Value of Creatin and Creatinin.

There is but a small amount of direct experimental evidence as yet recorded bearing on the fate of creatin or creatinin introduced as such into the animal organism.

Ph. Munk (*Deut. Klinik*, 1862, p. 299), determined urea and creatinin in the urine of dogs when 2 grms. of creatin was injected into a vein, and under normal conditions. He concluded that the injection of the creatin increased (certainly) the amount of creatinin and (doubtfully) the amount of urea excreted. He did not determine whether

any unaltered creatin was excreted. He also experimented to a very limited extent upon himself, taking by the mouth a rather small quantity of creatin, and reached similar results. Thus on a mixed diet he found in the urine when no creatin was taken 16 to 20.5 grms. urea, and 0.77 to 1.23 grms. creatinin; when 5.5 grms. creatin was taken, 21.8 grms. urea, and 1.48 grms. creatinin. The amount of urea reported seems remarkably low, assuming it to represent the excretion of twenty-four hours, and the increase in the amount of both urea and creatinin excreted is not great, while the creatinin represents but a small part of the creatin taken.

Meissner (*Ztschr. rat. Med.*, 1865, Series 3, xxiv., p. 100; 1866, xxvi., p. 225), also injected solutions of creatin and creatinin into the blood of dogs and rabbits. He found that creatin was eliminated with great rapidity by the kidneys. Creatinin at first passed unchanged into the urine, but afterwards seemed to undergo decomposition, no more creatin or creatinin being found. In the case of the dogs with a meat diet he found creatin as well as creatinin always present in the urine. Voit criticised these experiments in which the substances were injected into the blood on the ground that *time* enough for metabolism is not given. In support of this objection he cited the fact that a large amount of sugar can be fully disposed of when it has been swallowed, while a few grms. injected into the blood will appear unchanged in the urine.

Voit (*Ztschr. Biol.*, 1868, iv., p. 77), made some experiments with dogs, taking into account the quantity of creatin contained in the meat with which they were fed, and aimed at showing that, as more creatin (in the form of creatinin) was recovered from the urine than was given in the meat food, the surplus must have been formed in the living body. He came to the conclusion that in the breaking up of proteids in the muscles a certain part of the nitrogen takes the form of creatin, and is given off as such (or, rather, for the most part changed to creatinin) in the urine. He deemed it very improbable that creatin is changed into urea, the amount of creatin in the urine rising or falling in proportion to the amount taken in in flesh food plus the amount due to proteid metabolism in the muscles.

Voit also made some experiments on a dog, adding creatin and creatinin in separate form to the food. He concluded that creatin and creatinin are not changed to urea, of which there was no sensible increase, but that the greater part is removed in the urine, the failure to recover all being perhaps due to a part being held back in the alimentary canal in consequence of sparing solubility. He also reported that he found under the administration of creatinin the urine may become temporarily alkaline, creatin being then given off, formed from creatinin in the body of the animal experimented on.

It may be added that Max Rubner (*Ztschr. Biol.*, xx., p. 265), found by direct experiment on a dog with a respiration apparatus that the flesh bases of meat extract have no influence on the elimination of carbon dioxide or the production of heat.

It seemed, therefore, that experiments were desirable which might throw further light on this debatable question of the relations of creatin and creatinin to the chemistry of animal life.

(To be continued).

Action of Sulphide of Ammonium on the Nitrated Aromatic Nitramines and Nitrosamines.—J. Pinnow and P. R. Oesterreich.—The authors show that the *p*- and *o*-nitrophenylmethyl nitrosamines are transformed by the action of sulphide of ammonium—with elimination of the nitro-group of the lateral chain—into nitromethylanilines, and the *o*-nitro *p*-tolylmethyl nitramine into amidotolylmethyl nitramine. When operating on the *p*-nitrophenylmethyl nitrosamine, the nitroso-group is eliminated.—*Berichte der Deutsch. Chem. Gesell.*

ON A TEST,
BY THE FREEZING-POINT METHOD,
OF THE
IONISATION COEFFICIENTS DETERMINED BY
THE CONDUCTIVITY METHOD,
FOR
SOLUTIONS CONTAINING POTASSIUM AND
SODIUM SULPHATES.*

By E. H. ARCHIBALD, M.Sc.,
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THE experiments described below were undertaken, at the suggestion of Prof. J. G. MacGregor, for the purpose of testing the values of the ionisation coefficients obtained by means of his graphical method (*Trans. N.S. Inst. Sci.*, 1895-6, ix., 101), in the case of a mixture of solutions of two electrolytes with a common ion, by employing them in the calculation of the depression of the freezing-point, and comparing the calculated values with values obtained by experiment.

The time at my disposal was very limited, and in consequence I was able to make the test only in the case of equimolecular solutions of two electrolytes. Potassium and sodium sulphates were selected as the electrolytes, not because of their being the most suitable for the purpose, but because I had been observing their conductivity and had already obtained some of the requisite data.

As, in determining the depression of the freezing-point, the solutions must be at a temperature of about 0°C ., it was necessary that the ionisation coefficients should be determined for approximately the same temperature. Both the specific conductivities of simple solutions of the two electrolytes throughout the range of concentration of the simple solutions used in preparing the mixtures, and their equivalent conductivities at infinite dilution, had therefore to be determined for 0°C ., as well as the depression of the freezing-point for the mixtures. In addition, in order to determine how closely the depression in the case of simple solutions can be calculated by means of ionisation coefficients determined by conductivity measurements, I observed the depression in the case of simple solutions also.

The work involved in making the desired test therefore included the following:—(1) The purification or testing of the materials; (2) the preparation and analysis of series of simple solutions and the preparation of the mixtures; (3) the measurement of the conductivity of series of simple solutions at 0°C .; (4) the determination of the equivalent conductivity at 0°C . of the two electrolytes at infinite dilution; (5) the calculation of the ionisation coefficients of the simple solutions; (6) the measurement of the depression of the freezing-point for the simple solutions; (7) the calculation of the depression for the simple solutions by means of the ionisation coefficients obtained from the conductivity measurements; (8) the measurement of the depression of the freezing-point in the case of the mixtures; (9) the determination of the ionisation coefficients of the electrolytes in the mixtures; and (10) the calculation of the depression of the freezing-point of the mixtures by means of these coefficients.

The Materials.

The salts were obtained as chemically pure from Eimer and Amend of New York, and were re-crystallised carefully three times, after which treatment no appreciable impurities could be detected.

The water used was purified by Hulett's method (*Journ. Phys. Chem.*, 1896, i., 91), except that a block tin condenser was employed instead of a platinum one. Portions of the distillate were treated in the same manner as to exposure to air, &c., as a solution would be, and their

conductivity measured. It was found to vary from 0.88×10^{-10} to 0.96×10^{-10} , expressed in terms of the conductivity of mercury at 0°C . It was kept in bottles which had been used for this purpose for several years.

Preparation and Analyses of Solutions.

The potassium sulphate solutions were prepared by adding to water a known weight of anhydrous salt which had been dried to constant weight in an air-bath, so as to form a known volume of solution at 18°C . In the case of the sodium sulphate, a solution was prepared, and analysed by gravimetric determination of the sulphuric acid present in a known volume of solution. Several solutions of both salts of different concentrations were prepared in the above manner, and others were prepared from these by addition of water, their concentrations being calculated. Check analyses were made whenever any portion had gone through two or three dilutions, and if found necessary the calculated concentrations were corrected from these results.

The complex solutions were prepared by mixing equal volumes of the constituent solutions at 18°C ., the same precautions being observed for securing equality of volume of the constituents as are described in a former paper communicated to the Institute on the conductivity of these salts (*Trans. N. S. Inst. Sci.*, 1897-8, ix., 291).

The concentrations of the solutions at 18°C . would, of course, be slightly less than their concentrations at 0°C ., but with solutions as dilute as those which I used, the difference could hardly affect the third significant figure.* I have therefore regarded the concentrations at the two temperatures as the same.

As the method of calculation required a knowledge of any appreciable change of volume which might occur on mixing, simple solutions of each of the salts were prepared, and density determinations were made of such solutions before and after mixing. These measurements were carried out at 18°C . with Oswald's form of Sprengel's pycnometer. They might be in error by about 5 in the fifth decimal place. No change of volume was found to occur on preparing the most concentrated mixture examined, which would appreciably affect its concentration with respect to the two electrolytes, when calculated on the assumption that no such change of volume occurred.

Method of Measuring Conductivity.

The method used was Kohlrausch's telephone method, and the apparatus was the same as described in the paper just referred to.

Two electrolytic cells were used, one for strong, the other for more dilute solutions. The first was U-shaped of the form shown by Ostwald in his "Physico-Chemical Measurements," p. 226, Fig. 178. The second was cylindrical, about 14 c.m. long, with an internal diameter of 3.3 c.m. It was provided with circular electrodes of stout platinum foil not easily bent. The stout wire supports of these electrodes were fused into glass tubes which passed through, and were sealed to, the ebonite cover of the cell. The electrodes were kept firmly in position by means of a rubber band passing over the cover and around the bottom of the cell. This cell being long and of the same diameter throughout, could, by variation of the distance between the electrodes, be used for solutions extending through a wide range of dilution.

The platinising of the electrodes was carried out as described in the paper cited above.

The water-bath described in the above paper was used for these experiments also, modified, however, when working at 0°C . as follows:—A cylindrical screen made

* From the *Transactions of the Nova Scotian Institute of Science*, vol. x., Session 1898-99.

* From Forch's observations on the thermal expansion of solutions of potassium sulphate (*Wied. Ann.*, 1895, lv., 100), and Marignac's on sodium sulphate (*Ann. Chim. Phys.*, 1871 (4), xxii., 385), I find that the difference of temperature referred to would affect the third significant figure of the concentrations only in the case of the stronger solutions examined, and in the case of these only to the extent of 1 or 2 units.—J. G. M.

of wire gauze about 15 c.m. in diameter was hung from a support so as to reach from the top, to within 6 or 8 c.m. of the bottom, of the bath. Inside this, the electrolytic cell containing the solution to be measured was placed, while outside was a mixture of snow and a very little sodium chloride. The screen thus prevented the snow from coming into contact with the cell, while the water around it could be thoroughly stirred. By varying the amount of salt the temperature could be kept within a twentieth of a degree of zero for half an hour at a time. An error of this amount in the determination of the temperature of the solution would cause an error of about 0.1 per cent in the determination of the resistance. The temperature of the room in which the observations were made was from 2° to 5° C. That one might be sure that the temperature of the solution to be measured had come to be that of the bath, measurements of the resistance were made at short intervals, and that reading taken which was found to be constant for successive intervals. The thermometer used was graduated to tenths of a degree centigrade, and could easily be read to twentieths. Its errors had recently been determined at the Physikalisch-Technische Reichsanstalt, Berlin.

The factor for reducing the observed conductivities to mercury units was found by plotting observed conductivities at 18° C. against concentrations, reading off from these curves the conductivity values for concentrations examined by Kohlrausch, and comparing them with his results. The value thus obtained was found to be the same for each salt, and to be practically constant throughout the concentration range of my experiments. As the cell was of glass the reduction factor would not be appreciably different at 0° C. from what it was found to be at 18° C. To make sure that no change occurred in the position of the electrodes during the course of the experiments that would appreciably affect the reduction factor, every second or third solution was measured at 18° C. before reducing its temperature to 0° C., and the value of the conductivity obtained was compared with that previously obtained at the same temperature.

(To be continued).

NOTICES OF BOOKS.

An Introduction to the Carbon Compounds. By R. H. ADIE, M.A., B.Sc. London: W. B. Clive, University Correspondence College Press. 1899. Pp. 90.

WITH the idea of enabling students to have a better grasp of physiological subjects, with regard to both animal and plant life, the author has endeavoured in this book to lead the reader to a consideration of the more important groups of carbon compounds, without laying too great stress on the general methods; the importance of understanding the chemical changes brought about by living matter cannot be overrated, and it must not be forgotten that the chemistry of organised matter is just as much a matter for experiment as is inorganic chemistry.

The course followed in this volume comprises the hydrocarbons, including the paraffin series, ethylene, acetylene, and benzene, the haloid derivatives, alcohols, ethers, aldehydes, sugars, acids, &c. The theoretical descriptions are followed by experiments which will help to impress the facts on the mind of the student.

Action of Ferric Chloride and Bromide on some Aromatic Carbides, and on their Halogen Substitution Derivatives.—V. Thomas.—In a previous paper the author published the beginning of this research. From the product of the action of ferric chloride on paradibromobenzene he now isolates two new bromotrichlorobenzenes, one of which melts at 93° with formula $C_6H_2Cl_3Br$, and the other melting at 138° and having the formula $C_6H_2Cl_3Br$.—*Comptes Rendus*, cxxviii., No 26.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxviii., No. 26, June 26, 1899.

Preparation of Fluorine by Electrolysis in a Copper Apparatus.—Henri Moissan.—Instead of using the expensive platinum apparatus hitherto employed, the author substitutes one of copper. Copper is less attacked by fluorine than most metals, owing to the fact that the copper becomes coated with a thin layer of copper fluoride. This substance is insoluble in hydrofluoric acid, and so prevents further action. The temperature must not be too low to prevent the union of the hydrofluoric acid and the alkaline fluoride from taking place throughout the whole mass. By means of this apparatus a continuous current of fluorine gas can be obtained.

Constitution of the Oxides of the Rare Earths.—G. Wyrouboff and A. Verneuil.—In a previous paper, the authors pointed out that no argument exists which is in favour of the hitherto accepted trivalence of cerium, lanthanum, and didymium, and the tetravalence of thorium. The investigation of the formation of various complex salts of cerium and thorium lead to the suggestion that the oxides of these two metals have the formulæ $(CeO)_3$ and $(ThO)_4$. In each case one of the CeO and ThO groups differ in function from the other two.

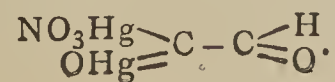
Preparation of Phenyl-chlorocarbonates.—E. Barral and Albert Morel.—The authors prepare these compounds by the action of a solution of carbonyl chloride in toluene on an aqueous solution of the sodium compound of phenols. The temperature at which the reaction takes place should not be allowed to exceed 40–50°; for above this temperature decomposition ensues and the symmetrical phenyl carbonate is produced.

Cerine and Friedeline.—C. Istrati and A. Ostrogovich.—The substance previously extracted from cork by one of the authors is subjected to fractional dissolution in, and crystallisation from, chloroform. By this means it is separated into two distinct compounds: cerine, $C_{27}H_{44}O_2$; and friedeline, $C_{43}H_{70}O_2$.

New Reactions of Indolic Bases and Albumenoid Compounds.—Julius Gnezdä.—If indol or any of its derivatives are heated with excess of oxalic acid a purple colouration is produced. A similar reaction is given by albumen, peptones, and gelatin. Various other dibasic acids may be used instead of oxalic acids. Other colour reactions occur by means of hydrofluoric and hydrofluosilicic acids, which the author describes.

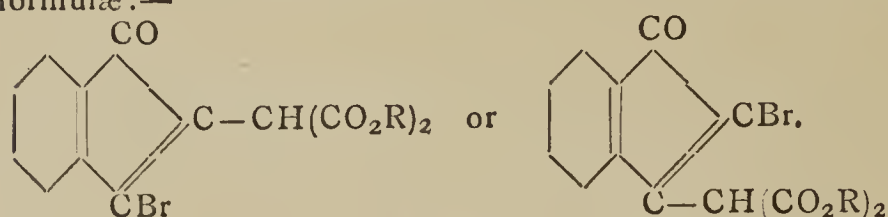
Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxi., November 28, 1898.

Action of Acetylene on Nitrate of Mercury.—K. A. Hofmann.—The author has recently announced that acetaldehyde furnishes with an aqueous solution of mercuric nitrate a white crystalline compound corresponding to the formula $C_2Hg_2NO_4H$. This compound has also been obtained by means of acetylene, which is a further proof of the transformation of this substance into acetaldehyde. The author finds that by reacting with acetylene on the warm solution of mercuric nitrate according to Erdmann's method, a mercuric compound of acetaldehyde or of vinoxylic alcohol is formed, which, after having been purified by means of dilute nitric acid, corresponds to the formula $C_2Hg_3NO_5H$, which can no doubt be developed as follows:—



Action of Hydrate of Hydrazine on the Phenols.—L. Hoffmann.—During a research on the preparation of the derivatives of hydrazine containing phosphorus, the author found that the naphthols, under the action of hydrate of hydrazine, are transformed into naphthylhydrazines, and that in the same manner phenol gives, at a high temperature, small quantities of phenylhydrazine. With α - and β -naphthol the reaction takes place by heating with excess of hydrate of hydrazine for six hours to 160° in a sealed tube; it can be expressed by the equation $C_{10}H_7OH + NH_2.NH_2 = C_{10}H_7NH.NH_2 + H_2O$. With phenol it is necessary to heat up to 220° , but a small quantity only of phenylhydrazine only is formed.

Coloured Reactions of the Indones and Quinones with the Derivatives of Malonic Acid.—C. Liebermann.—It is well known that a coloured reaction takes place when the soda compound of malonic ether is made to react on dichlorindone. The author has now studied this reaction with dibromindone, and he found that a compound is formed corresponding to one of the following formulæ:—



He has since observed that this very characteristic reaction is susceptible of being generalised. Following this up, he has been led to examine the action of malonic ether on 2:3-dibrom- α -naphthoquinone, and he finds that it gives a magnificent blue colouration. The corresponding derivative of β -naphthoquinone gives a greenish blue colouration; the monobromo- and monochloro- β -naphthoquinone behave in an analogous manner. All these compounds are very unstable in alkaline solution. He has also observed that the soda compound of malonic ether acts on the non-substituted quinones. With α -naphthoquinone he obtained a bluish green, and with β -naphthoquinone a red solution. The fact that the same reaction is observed with the indones is interesting, inasmuch as it confirms the intimate relations which exist between the group of quinones and of the indones.

Some Derivatives of *o*-Tolunitrile.—W. Landsberger.—The author has studied the nitration of *o*-tolunitrile which gave 4-nitro-*o*-tolunitrile, fusing at 105° , of which the amide occurs in brilliant needles fusible at 173° , and the product of reduction, the amino-*o*-tolunitrile, in needles fusing at 88° . He also describes the chlorhydrate, the picrate, and the double salt of platinum. He further describes a research made on the action of the soda compounds of the methyl- and the ethyl-acetacetic ethers on the chloride of *o*-cyanbenzyl, and gives an account of the preparation and properties of several compounds.

Peracetylation of Phenacetine.—A. Bistrzycki and F. Ulffers.—One of the authors showed some time ago that the diacetanilide which forms on heating aniline with a large excess of acetic anhydride does not differ in its physiological properties from monoacetanilide (antifebrine). He has now repeated the experiment with phenetidine, of which the monoacetyl derivative (phenacetine) is a well-known medicine. The diacetphenetidide, which he prepared by heating phenacetine twice with a large excess of acetic anhydride, crystallises in ligroin in colourless needles. Although but slightly soluble in cold water, it is more so than phenacetine. The diacetphenetidide appears, even in the smallest doses, to produce the same physiological effects as phenacetine; in equal doses it acts in a much stronger manner, but the effect does not last so long. The authors also describe another derivative of phenetidine, viz., chloracet-*p*-phenetide, $C_2H_5O.C_6H_4.NH.COCH_2Cl$, obtained by the action of chloride of chloracetyl on *p*-phenetidine in solution in toluene; this compound occurs in prisms or in leaflets fusible at $145-146^\circ$.

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S. CHAFFERS, Registrar.

UNIVERSITY COLLEGE, BRISTOL.

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PHOTOGRAPHIC RESEARCHES ON PHOSPHORESCENT SPECTRA: ON VICTORIUM, A NEW ELEMENT ASSOCIATED WITH YTTRIUM.*

By Sir WILLIAM CROOKES, F.R.S.

It has long been known that certain substances enclosed in a vacuous glass bulb phosphoresce brightly when submitted to molecular bombardment from the negative pole of an induction coil. The ruby, emerald, diamond, alumina, yttria, samaria, and a large class of earthy oxides and sulphides, emit light under these circumstances. Examined in a spectroscope the light from some of these bodies gives an almost continuous spectrum, while that from others, such as alumina, yttria, and samaria, gives spectra of more or less sharp bands and lines. Since 1879 I have been working on these phosphorescent spectra, chiefly in connection with the earths of the yttria group, and by chemical fractionation I have succeeded in separating from this group bodies whose phosphorescent spectra consist chiefly of single groups of lines, other groups being absent. For the last six years the research has been extended beyond the visible spectrum, and photographs of the ultra-violet portion of the spectra are now being taken with a spectrograph with a complete quartz train. Some of the results of this investigation were exhibited at the Soirée of the Royal Society on the 3rd of May. A preliminary mention of the discovery of a new element was made in my Address to the British Association in September last, when I provisionally called it Monium; but for several reasons I now consider the name Victorium more appropriate.

The complicated scheme of fractionation carried on for so many years is illustrated in the accompanying diagram. This must be considered only as an indication of the methods employed, and not as an actual representation of every operation through which the material has passed. Crude yttria, from samarskite, gadolinite, cerite, and other similar minerals, is the raw material. The first operation is to free it roughly from earths of the cerium group—an operation effected by taking advantage of the fact that the double sulphates of potassium and the yttrium metals are easily soluble in saturated potassium sulphate solution, while the corresponding double sulphates of the cerium group of metals are difficultly soluble.

After this preliminary treatment, the crude yttria is converted into nitrate, represented by the topmost circle on the diagram. The nitrate is exposed to heat until it fuses to a clear liquid, care being taken to distribute the heat uniformly through the mass. Presently the liquid mass commences to decompose, giving off red vapours. After this has proceeded for a little time, the fused mass is carefully poured into water, and the liquid well boiled. A white precipitate of basic nitrate forms, while the undecomposed nitrates remain in solution. These are separated by filtration—the precipitate going to the right and the solution to the left. The basic nitrate is dissolved in nitric acid, and the right and left solutions are then evaporated to dryness and fused as before. Partial decomposition by heat again divides each of these portions into two lots, soluble and insoluble. The soluble from the left-hand lot goes still further to the left, and its insoluble portion to the right. The soluble from the right-hand portion goes to the left, where it mixes with the insoluble from the other portion, while its

insoluble goes still further to the right. This series of operations is continued for as long a time as the material will hold out.* From a description the process seems to be more complicated than it really is, but a study of the diagram and the direction of the arrows make it clear. The number of times this operation is performed varies with each lot of earth fractionated. The portions submitted to fusion rapidly diminish in quantity, and the operation is continued until the material becomes too scanty.

The last horizontal line of fractions, spectroscopically examined in a radiant matter tube, shows differences in the visible spectrum. For many years I recorded these differences in coloured drawings, which have served on several occasions to illustrate papers before this Society.† In the year 1893 I commenced to record the differences between the various spectra by photographing them in a spectrograph having a complete quartz train, and since that time attention has chiefly been directed to the variations in the number, character, and positions of the lines and bands in the ultra-violet spectrum; these are more striking than those which are visible, and as they are self-recording results are more rapidly attained. A description of this instrument is given further on.

On placing the photographed spectra of one of the horizontal lines of earths in order, several differences are detected. One striking difference is seen in the behaviour of a group of lines in the ultra-violet. It is nearly absent in the end fractions, gradually becoming stronger towards the middle, and attaining a maximum in the fractions situate about two-thirds towards the right. This shows that at least three different bodies are present: one, the great bulk, having a nitrate difficult to decompose; another whose nitrate is easiest to decompose; and a third body, occupying an intermediate position, whose nitrate decomposition occurs at temperatures between that required by the others, but nearer that of the nitrate easiest decomposed.

The above method of fractionation is not so effectual if more than two bodies are present. In that case the process fails, in any reasonable time, to yield practically pure specimens of more than two out of a group of closely allied earths. Thus, if there are three earths—say, A, B, and C—whose positions in reference to the chemical process employed are in the written order of sequence, we may get a specimen of A as nearly as we please free from B and C, and a specimen of C as nearly as we please free from A and B, but we cannot get a specimen of B practically free from A and C. The law seems to be that to obtain practically pure specimens of three closely allied earths, it is essential to have recourse to at least two different chemical processes. The mere continued repetition of the same process will not do, unless indeed the operations are repeated such a vast number of times as to make the approximate expressions no longer applicable, even though the substances are chemically very close.

For this and other reasons it is advisable to change the method of fractionation after one process has been in operation for some time. It is evident that any process of fusion, crystallisation, or precipitation can only divide the mass of material into two parts, a soluble and insoluble portion, crystals and mother liquor; and after a time a balance of affinities seems to be established, and further fractionation appears to do little good. It is better then to change the operation.

Following the diagrammatic scheme, the portions of earths containing most victorium are collected together and fractionated by the crystallisation of the oxalates from a solution strongly acidulated with nitric acid in the following manner:—

To a boiling acid solution of the nitrate a small quantity

* A Paper read before the Royal Society, May 4, 1899.

* "On the Methods of Chemical Fractionation," British Association, Birmingham Meeting, 1886; CHEMICAL NEWS, vol. liv., p. 131.
† "On some New Elements in Gadolinite and Samarskite Detected Spectroscopically" (Roy. Soc. Proc., No. 245, 1886, vol. xl., p. 502).

of hot solution of oxalic acid is added. The solution remains clear, and it is only after vigorous stirring that a small quantity of insoluble oxalate is formed. The whole is thrown on a hot-water filter and slightly washed with boiling water. To the boiling filtrate a fresh lot of hot solution of oxalic acid is added, and stirred till more insoluble oxalate comes down. This is again filtered off, and the operations of precipitating, stirring, filtering, and washing are repeated, always keeping the temperature as near the boiling-point as possible, until the whole of the earths are precipitated. Generally the initial earth is divided by this method of fractionation into from six to twelve portions. Each of these oxalates is dried, ignited, dissolved in nitric acid, and the above-described operations repeated. Photo-spectroscopic tests are constantly taken during the progress of this fractionation, and portions are mixed together according to the data thus obtained, as shown on the diagram by the lines joining the fractions. The object being to avoid lateral spreading as much as possible, and, while concentrating the special line-giving earth, to prevent its too great diffusion over a large number of fractions. When the fractionation by the oxalate method has proceeded for a considerable time, the fractions rich in victorium are collected together and submitted to another mode of treatment.

These fractions are converted into nitrates, and a small quantity is thrown out by partial decomposition by heat, according to the method already described. The filtrate is evaporated to dryness and again fused, so as to throw out a little more. This operation is repeated as long as any soluble nitrate is left. Generally from six to twelve portions are thus obtained. These form a regular series, differing according to the stability of the nitrate under heat. On testing, the victorium is found to concentrate in the centre portions, being less easily decomposed than the earths of the cerium group, and more easily decomposed than those of the yttrium group.

The fractions rich in victorium are converted into sulphates and mixed with a hot saturated solution of potassium sulphate. The precipitate is dissolved in boiling water and mixed with a further quantity of solution of potassium sulphate. This produces a small quantity of a precipitate. The filtrate from the first precipitate is also mixed with fresh potassium sulphate, and the operations are repeated, mixing the centre solutions to one lot and the side solutions to another, as shown by the lines on the diagram. It is found on photo-spectroscopic examination that the earths thrown out on each side are poorest in victorium, whilst those in the middle are richest. After a time no further concentration is effected in this manner, all the earths that can be removed as being more or less soluble in potassium sulphate having been eliminated.

In thus describing the method of fractionation, my object has been not so much to give a description of the plan actually carried out in the laboratory—for the details have varied with each operation—but to give an intelligible idea of the general manner in which a very complicated operation is effected. In the diagram I am supposing that one particular substance, victorium, is to be separated, and I have endeavoured to show its migrations and gradual concentration as the work progresses, by tinting the fractions where it mostly would concentrate; the depth of tint representing the amount of concentration.

In the purest condition yet obtained victoria is an earth of a pale brown colour, easily soluble in acids. It is less basic than yttria and more basic than most of the earths of the terbia group. In chemical characters it differs in many respects from yttria. From a hot nitric acid solution victorium oxalate precipitates before yttrium oxalate and after terbium oxalate. On fractional precipitation with potassium sulphate the double sulphate of victorium and potassium is seen to be less soluble than the corresponding yttrium salt, and more soluble than the double sulphates of potassium and the terbium and cerium groups. Victorium nitrate is a little more easily decom-

posed by heat than yttrium nitrate, but the difference is not sufficient to make this reaction a good means of separating victorium and yttrium. Fusing the nitrates can, however, be employed advantageously to separate mixed victoria and yttria from the bulk of their associated earths.

On the assumption that the oxide has the composition Vc_2O_3 , the atomic weight of victorium is apparently not far from 117.

The photographed phosphorescent spectrum of victoria consists of a pair of strong lines at about λ 3120 and 3117; other fainter lines are at 3219, 3064, and 3060. Frequently the pair at 3120 and 3117 merge into one, but occasionally I have seen them quite distinct. The presence or absence of other earths has much influence on the sharpness of lines in phosphorescent spectra, and it is probable that these lines will be sharp and distinct when victoria is obtained quite free from its associates.

The best material for phosphorescing in the radiant matter tube is not the earth itself, but the anhydrous sulphate formed by heating the earth with strong sulphuric acid and driving off the excess of acid at a red heat. The sulphate thus produced, probably also containing some basic sulphate, is powdered and introduced into a bulb tube furnished with a quartz window, and a pair of thick aluminium poles sealed into the glass with stout platinum wires. The tube is well exhausted, keeping the current from a good induction coil going all the time. The pumping and sparking must continue until the earth glows with a pure light free from haze or cloudiness, and continues so to glow during the passage of the current without deterioration. The exposure in the spectrograph usually occupies an hour.

I give a diagrammatic plan of the two-prism spectrograph used in this research. It is furnished with two quartz prisms, quartz lenses, and condensers. The slit jaws are of quartz, cut and polished according to the method I described in the CHEMICAL NEWS, vol. lxxi., p. 175, April 11, 1895.

The prisms are made in two halves according to Cornu's plan; one half of each being right-handed and the other half left-handed. One of the lenses also is right-handed and the other left-handed. By this device the effect of double refraction is so completely neutralised that with a five-prism instrument it is impossible, under high magnifying power, to detect any duplication of the lines.

The lenses are each of 52 m.m. diameter and 350 m.m. focus. The focus of the least refrangible rays is longer than that of the most refrangible rays, and the sensitive film must therefore be set at an angle to get the extreme rays into focus at the same time. But this alone is not sufficient. The focal plane is not a flat surface, but is curved, and the film must therefore be curved,* and it is only when both these conditions are fulfilled that perfectly sharp images of spectral lines extending from the red to the high zinc line 2138.30 can be photographed on the same surface. Celluloid films are used, glass not being sufficiently flexible.

Using the middle position showing the whole spectrum on a plate, the angle is 40° , and the curvature is 190 m.m. radius.

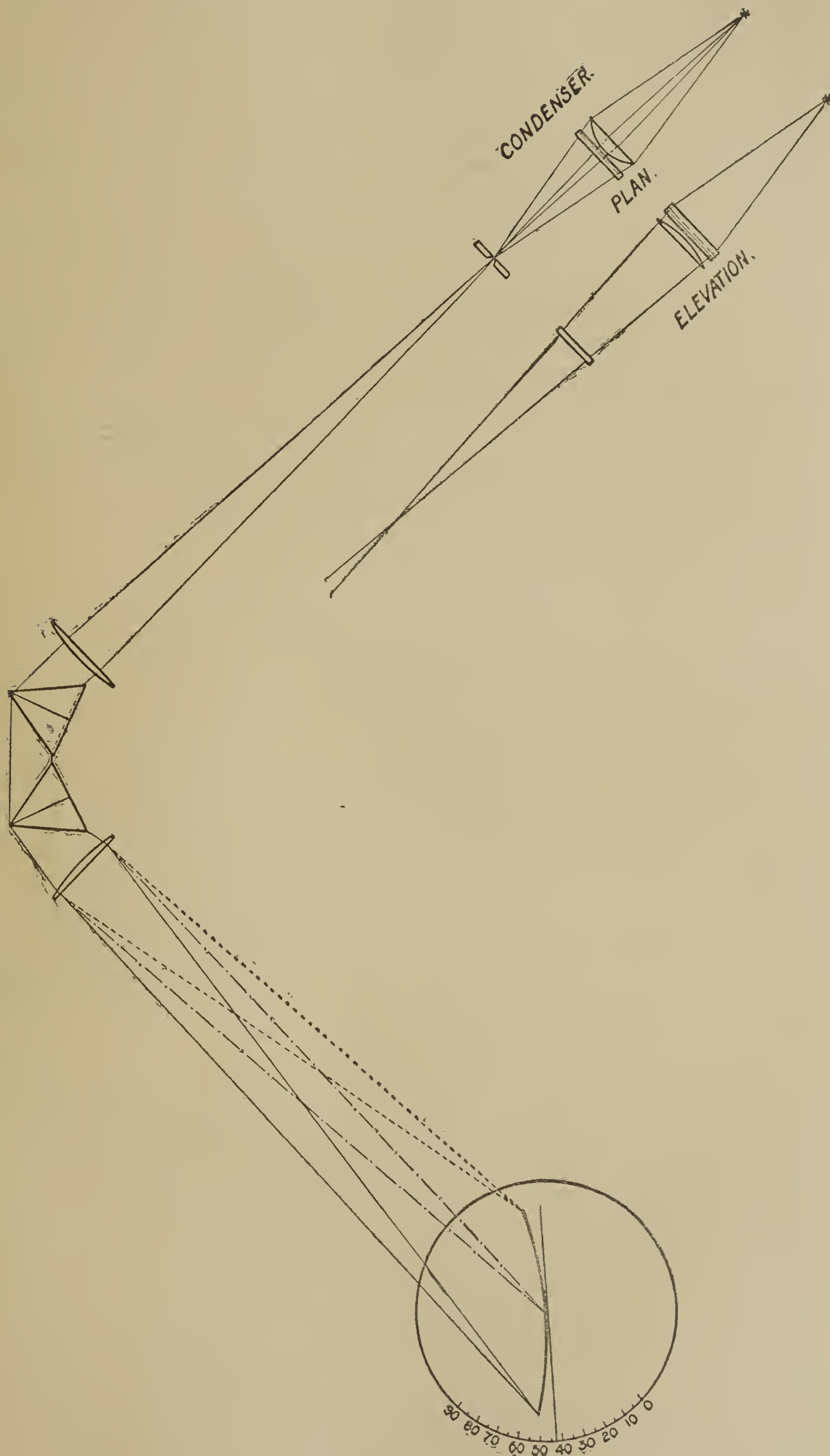
The condensers are of quartz, and are plano-cylindrical—one being double the focus of the other. The object of this, when spark-spectra are being photographed, is to concentrate on the slit a line instead of a point of light, as would be the case if ordinary lenses were used.

When photographing phosphorescent spectra—or, in fact, any spectra the wave-lengths of which are either unknown or require verification—I always photograph on the same film a standard spectrum, usually of an alloy of equal molecular weights of zinc, cadmium, tin, and mercury. This forms a hard, somewhat malleable alloy, giving throughout the whole photographic region lines

* CHEMICAL NEWS, vol. lxxii., p. 87, August 23, 1895; and vol. lxxiv., p. 259, November 27, 1896.

the wave-lengths of which are well known. The chief objection to this alloy is its volatility—the poles requiring frequent adjustment. Recently I have used pure iron for this purpose; this has the advantages of giving a great number of fine lines whose wave-lengths are accurately known, and not being very volatile, the poles do not

the other for the standard spectrum. In this way, without disturbing the instrument, the two spectra can be recorded on the plate one over the other; the overlap of 1 m.m. being in the optical centre of the train. The resulting negative is then transferred to a micrometer measuring machine of special construction,



rapidly wear away. If the poles are kept about 1 m.m. apart there is little or no interference from air lines.

The most simple method of applying the standard lines to an unknown spectrum is by the successive employment of two slightly overlapping diaphragms immediately behind the slit, one being used for the experimental and

having a screw of $\frac{1}{1000}$ of an inch pitch, and a means of accurately determining $\frac{1}{1000}$ of its revolution—thus measuring directly to the hundred-thousandth of an inch. In this way, in a five-prism spectrograph having lenses 700 m.m. focus, it is possible to determine wave-lengths of photographed lines to the sixth figure.

THE VOLUMETRIC ESTIMATION OF CARBON.

THE moist combustion process has made analysts familiar with the equation—



which represents the oxidation of carbon by chromic acid. Imbert and Compan's process (CHEM. NEWS, lxxix., 267), based on this reaction consists in measuring the excess of chromic acid added. This latter detail distinguishes it from similar processes in which the evolved CO_2 is generally either measured or absorbed and weighed.

Although the estimation of carbon depending on the measuring of the residual chromic acid strikes one as being something new, it can only be regarded as such in its application to elemental carbon as distinguished from carbon compounds. Certainly a significant and suggestive fact.

Cross and Bevan (*Journ. Chem. Soc.*, 1888, liii., 889), have investigated the combustion of cellulose compounds from the point of view of the oxidising substance by estimating the excess of chromic acid; and Phelps (CHEM. NEWS, lxxvi., 246), estimates carbon and oxygen simultaneously in a number of organic compounds by absorbing the evolved carbon dioxide and titrating the residual CrO_3 .

Cross and Bevan found that the gas evolved on heating a carbon compound along with chromic and sulphuric acids consists of CO and CO_2 , though in the more favourable tests the amount of the former was only some 2 or 3 per cent; they therefore measured the evolved gases in a graduated tube, a process altogether indifferent to the ratio $\frac{\text{CO}}{\text{CO}_2}$. Phelps, acting on Ludwig's observation that

contact of carbon monoxide with a mixture of chromic and sulphuric acids, especially when hot, results in the oxidation of that gas to carbon dioxide, contrived to retain the products of the oxidation in prolonged contact with the oxidising mixture, and obtained very satisfactory results by estimating the CO_2 gravimetrically.

The advantage of measuring the residual CrO_3 compared with any form of measuring the CO_2 is obvious; the operation is easier, and involves no expensive or delicate contrivances. It is, however, equally obvious that although only carbon compounds can produce carbon dioxide, quite a number of bodies other than carbon can effect the reduction of chromic acid, and the need to separate those bodies must frequently counterbalance what advantage the method has over those usually adopted. This limits the method to a certain class of carbon compounds.

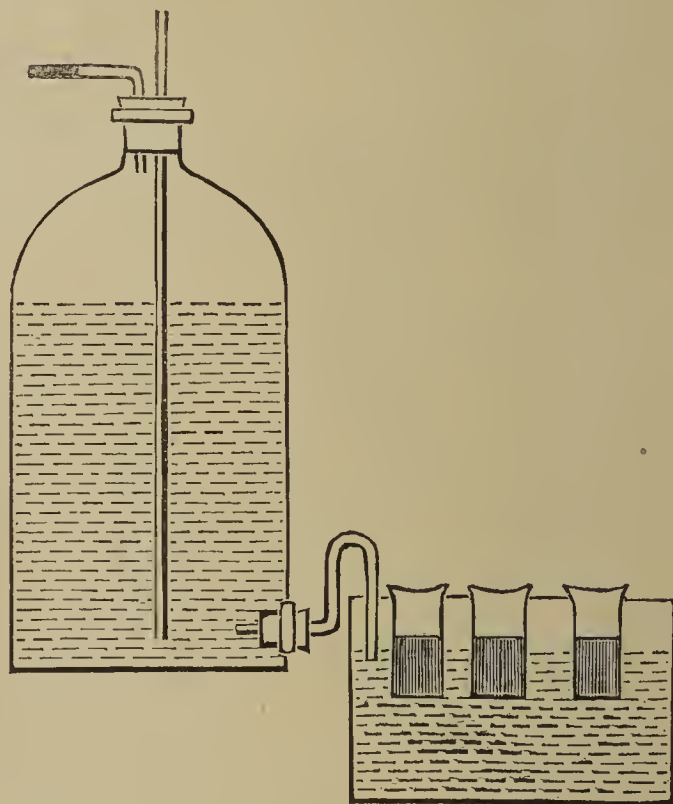
The application of the method to the estimation of carbon in steel illustrates its value, and indicates its limitations.

The carbon must be separated by treatment with any of the usual copper solutions, filtered off, and washed with a hot solution of dilute sulphuric acid until the washings no longer discharge a faint permanganate colouration. This is done to ensure the absence of ferrous and cuprous salts, and is very nearly successful. An examination of the carbonaceous residue and filter shows that the last traces of these salts are very difficult to remove. Besides carbon, hydrogen, and oxygen the residue contains (I refer only to ordinary steels), very small amounts of silica, sulphur, and phosphorus. The whole of these impurities, including the residual metallic salts, are of moment only in exceptional cases.

Instead of the seemingly roundabout means of estimating the excess of chromic acid adopted by Imbert and Compan most people would prefer to use ferrous sulphate or some other reducing agent which can be directly titrated by the bichromate used for the oxidation of the carbon. A solution of ferrous salt is so commonly used for other purposes where steel analysis is engaged in that in this connection it is as suitable a reagent as could be chosen.

A filter of asbestos, sand, or other non-oxidisable body must be used to separate the carbon, and it is necessary that during the final heating in the water-bath there should be more liquid than can be absorbed by the filtering medium. There must be enough, in fact, to permit free movement and ready admixture of the filter and oxidising solution, else the reaction, which is mainly active at this stage, is very much hindered. This difficulty is best avoided by making up a standard bichromate solution containing as much sulphuric acid as possible, short of precipitating the chromic acid. This will be about 500 or 600 c.c. per litre. Such a mixture may be heated in the water-bath without fear of decomposition; moreover, it is already so concentrated that a preliminary evaporation on the sand-bath, with its attendant dangers, is unnecessary. The carbon begins to be oxidised soon after placing in the bath, and it is completed for high percentage carbon steels in one or two hours. A sample digested for one hour* gave 1.15 per cent carbon; digested for two hours 1.18 per cent, and by combustion in oxygen and absorption of CO_2 1.18 per cent.

A convenient strength of bichromate solution is $\frac{1}{10}$ N. 25 c.c. of this solution oxidises 1 per cent of carbon from 3 grms. of steel. It is well known to be practicable even with N/10 bichromate solutions to titrate to 0.1 c.c., which under the above conditions is equivalent to only 0.001 per cent carbon, so that the errors of manipulation are of that insignificant kind which are so desirable in technical analysis.



For the analysis of pure carbon steels and pig-irons this process is worth serious consideration. It combines both speed and accuracy, and it is admirably suited for making estimations in batches, as is the daily practice in some works. The fact that the apparatus used is of the every-day order should commend it to the notice of those who have to do only an occasional sample as well as to instructors in laboratories where steel analysis is a subordinate subject.

During the oxidation of the carbon the asbestos entangles the CO_2 , and is floated to the surface of the liquid; this requires the solution to be stirred a few times, but it retains the gas for some time in contact with the oxidising mixture, and thus favours the complete oxidation of any escaping carbon monoxide. When the asbestos lies quietly in the solution, and a gentle stir causes no bubbles to appear, the reaction is complete. The figure shows a convenient water-bath, and constant level arrangement.

* This time can be shortened more than one-half by nearly constant stirring.

Some test analyses are:—

					Percentage carbon.	
					Dry combustion.	Vol. process.
Ordinary steels	1.18	1.18
"	"	0.94	0.95
"	"	0.75	0.76
"	"	0.52	0.52
"	"	0.43	0.42
"	"	0.29	0.29
Ferro-nickels, 26 per cent Ni	0.29	0.28
"	"	0.44	0.45
Pig-irons	4.02	4.03
"	4.27	4.17
"	4.15	4.08
"	3.71	3.80

With the exception of the pig-irons the results of the volumetric estimations are all that could be desired, and if we take account of the fact the carbon of the pigs was chiefly graphitic, and that the samples were weighed from a packet of drillings, the differences are not greater than might obtain were dry combustions duplicated, and may well be accredited to the difficulty of taking a perfect sample.

The graphitic carbon from the pig-irons was only slowly oxidised by the chromic and sulphuric acids at the temperature of a water-bath. It was found, however, that the $\frac{1}{10}$ N bichromate made up as described could be heated for several hours in a calcium chloride bath at 130° C. without appreciable decomposition; that in fact it could be heated up to (not kept at) its boiling point, 155° C., without decomposition, although, as Cross and Bevan show, a mixture of chromic acid and strong sulphuric acid is slowly decomposed by prolonged exposure at a much lower temperature (105° C.). Now, at 130° C. the graphitic carbon of the pig-irons is completely oxidised in about an hour and a half, and the carbon liberated from ordinary steel in about twenty minutes.

Carbon in Special Steels.

It is no longer possible to assume that carbon, silicon, manganese, sulphur, and phosphorus are the only elements worth noticing in the analysis of a piece of steel. Modern warfare and the requirements of the engineer have led to the introduction of chromium, nickel, aluminum, copper, and tungsten, while the experimental enquiries of the steel-maker are responsible for the occasional presence of several other elements. All these things make a complete analysis of a sample of steel no mean problem, as the process available for one sample may be hopelessly misleading when applied to another. A need, supplied by no text-book, and demanded by the painful experience of most analysts, is some concise statement of the influence exerted on common processes by elements which, though not common, are yet not so rare as to be considered curiosities.

Where the special element in a steel passes into solution when treated with the solution of copper salt the volumetric process for estimating carbon is available and trustworthy. Those elements which remain with the carbonaceous residue are apt to introduce error and may invalidate the process altogether.

Tungsten Steels.—Nearly if not all the tungsten is to be found in the washed carbonaceous residue. In titrating, the excess of ferrous sulphate once oxidised continually reappears. This appears to be due to the fact that the metallic tungsten is only very slowly attacked in the concentrated mixture of sulphuric and chromic acids used for the digestion, but is much more readily attacked when the solution is diluted for titration.

I find that although the results, using the $\frac{1}{10}$ N bichromate solution, are approximately correct after an hour's digestion, they become slowly higher and higher if the digestion is continued. To meet this difficulty the bichromate was powdered, weighed out, and mixed with the carbonaceous residue suspended in concentrated sulphuric

acid. Such a mixture of chromic and sulphuric acids has hardly any action on the tungsten, but, unfortunately, it does not by any means so readily oxidise the carbon liberated from combination with the iron. This point is again referred to below.

If a definite answer must be given to the enquiry, whether or not the volumetric process is available for tungsten steels, it can be said that it is, but in a somewhat limited and empirical degree. If no graphitic carbon is present, and the digestion be continued only until the asbestos sinks into the solution, and few or no bubbles appear on gentle stirring, the results will be only a few hundredths per cent out. If the digestion be made over several hours in a concentrated sulphuric solution the results are accurate, or only slightly high. In either case the digested solution should be rapidly passed through an asbestos filter, so as to keep the tungsten out of the solution titrated. Or again, after oxidising the carbon the solution may be diluted several times with water, and left to complete the oxidation of the tungsten by gentle boiling; the amount of tungsten being otherwise determined, it may be allowed for on the assumption that $2\text{CrO}_3 + \text{W} = \text{Cr}_2\text{O}_3 + \text{WO}_3$ expresses the reaction; that is, one atom of carbon reduces as much chromic acid as 10.22 atoms of tungsten. Some very good results have been obtained in this way, but the process is a slow one, and is obviously of no value technically.

From the numerous experiments summarised in the two preceding paragraphs, it appeared that concentrated sulphuric acid along with chromic acid was a less effective oxidiser of combined carbon than a more dilute solution, and that the reverse was true of graphitic carbon. Acting on the principle that an impression, however strong, is less satisfying than a demonstrated fact, the following experiments were made:—

The carbon from 3 grms. of a 1.18 per cent carbon steel was digested with equal amounts of potassium bichromate in equal volumes of—(A) strong sulphuric acid. and (B) dilute, half and half, sulphuric acid. Also, the residue from 1½ grms. of pig-iron (total carbon 4.15, graphite 3.41 per cent) was similarly digested. The presence of combined carbon in the pig-iron favours the weaker solution, the results were—

Combined Carbon.				
			A.	B.
			Per cent.	Per cent.
Digested one hour..	0.65	1.19
Digested two hours	0.73	1.19
Graphitic Carbon.				
Digested one hour..	3.58	2.57
Digested two hours	3.70	3.11

These results have considerable interest in connection with the oxidation of carbon with chromic and sulphuric acid in the ordinary moist combustion process. In text-book descriptions the aim appears to be to have the sulphuric acid in as concentrated a form as possible, and to heat the mixture until fumes of sulphuric anhydride are evolved. The fumes are a source of danger, in that they pass the purifying train and are, partially at least, absorbed in the potash bulbs. It is hardly possible to resist the conclusion that the carbon would be as readily—or generally, more readily—oxidised by a chromic acid solution containing only about 50 per cent sulphuric acid, which could be raised to boiling without any appreciable evolution of sulphuric anhydride. The only fear to be entertained is that the $\frac{\text{CO}}{\text{CO}_2}$ ratio might be increased; this,

however, is matter for experiment rather than speculation. Observations covering this point, and the most effective percentage of sulphuric acid to use for this particular purpose, are being made.

Molybdenum Steels.—Molybdenum does not interfere, although it partially accompanies the carbon. In neither

of the samples examined containing (A) 3 and (B) 8 per cent of molybdenum respectively was there any indication of a reducing action after the diluted solution had been titrated, as is the case with tungsten steels.

	C per cent grav.	C per cent vol.
A	0.98	0.99 and 0.98
B	3.73	3.72
C*	1.28	1.26

* Contains 3 per cent each of Mo and W.

Chrome Steels.—Chromium is said to exist in the carbonaceous residue as a double carbide of chromium and iron. Both these metals exert a reducing action on the chromic acid, so that anything but traces of chromium completely invalidates the method. The process may, however, be of service in determining the constitution of the carbonaceous residues from chrome steels.

J. T.

THE PHYSIOLOGICAL EFFECT OF CREATIN AND CREATININ, AND THEIR VALUE AS NUTRIENTS.*

By J. W. MALLET, M.D., LL.D.,
Professor of Chemistry in the University of Virginia.

(Continued from p. 45).

Materials Employed in the Present Investigation.

A GOOD deal was hoped from the use in experiment of larger quantities of the flesh bases in a state of purity than had previously been used, so that from the methods (necessarily not rigorously exact) of determining these substances as eliminated in the urine, results of a fairly decisive character might be obtained. The writer was fortunate enough (thanks to the kindness of a friend and former pupil, now connected with a firm preparing a well-known meat extract) to possess several hundred grms. each of almost chemically pure creatin and creatinin. These were very carefully purified further and re-crystallised, and furnished abundant material for the physiological experiments undertaken. They were quite free from mineral impurity of any kind. Each was tested for the presence of the other, and, by the fractional use of solvents, each was ascertained to be quite uniform in character.

The general properties of the creatin and creatinin so prepared were found to agree in general with the description given in the text-books, but a few special points of detail may be noted.

According to Liebig's description creatin "has a somewhat bitter taste, and scratches in the throat," while "creatinin in the state of concentrated solution has a caustic taste like that of dilute ammonia." Both of these substances as prepared by the author, when taken into the mouth in large quantity and swallowed with a little pure water, had a bitter taste, not very strong or disagreeable. This taste was comparatively slight in the case of creatin, and much more marked in that of creatinin, as might be expected from their different degrees of solubility.

The statements of Liebig and G. S. Johnson do not agree in regard to the solubility of creatinin in alcohol, the former finding it three times as soluble as did the latter. My determinations gave the following results:—100 grms. of 90 per cent ethyl alcohol dissolved 0.018 gm. of creatin or 0.454 gm. of creatinin at 19.2° C. Under these conditions, therefore, creatinin is more than twenty-five times as soluble as creatin. For the analytical separations to be made it was important to know also the solubility of urea in alcohol of the strength employed. On the authority of Prout it is stated that one

part of urea dissolves in five parts of alcohol of specific gravity 0.816 in the cold. I found that 100 grms. of 90 per cent alcohol dissolved 11.526 grms. of pure urea at 19.2° C., so that under these conditions it is more than twenty-four times as soluble as creatinin.

Some discrepancy has also been observed in the recorded statements as to the reactions of these flesh bases with litmus paper. According to the original observation of Chevreul, uncontradicted by later experimenters, creatin is neutral to vegetable colours, while Liebig and others have reported creatinin as distinctly alkaline, changing red litmus to blue and reddening turmeric. However, Salkowski found that a strongly alkaline sample left an alkaline ash on ignition, and that pure creatinin was quite free from alkaline reaction. The creatin used by me was quite neutral to litmus paper; the creatinin, although free from ash, gave an extremely faint, scarcely perceptible, alkaline reaction.

In view of the readiness with which creatin may be converted into creatinin, and *vice versa*, and in view also of the fact that for the purposes of this investigation they would have to be sought for and determined in the presence of the urea of urine, the behaviour of creatin, creatinin, and urea with reagents had to be examined. In this direction, also, results were obtained not altogether in accord with the statements of some of the text-books in general use. Thus, Allen (A. H. Allen; "Commercial Organic Analysis," vol. iii., Pt. III., p. 287), says: "Creatin is also distinguished from creatinin by being unprecipitated by a solution of phosphotungstic acid in presence of hydrochloric acid."

Using fairly strong aqueous solutions of the flesh bases, I found that the hydrochloric acid solution of phosphotungstic acid gave with creatin a small crystalline precipitate, forming gradually; with creatinin also a precipitate, but more copious, and forming more promptly.

In O. Hammarsten's "Text-book of Physiological Chemistry" (Authorised Translation, by J. A. Mandel, p. 348), the statement is made in reference to creatinin that "it is precipitated like urea, with mercuric-nitrate solution." I found that even the most concentrated aqueous solution of creatin or creatinin gave no precipitate with a solution of mercuric nitrate containing just enough free nitric acid to make it clear, while the reagent gave an abundant precipitate with a solution of urea. If to the mixture of creatin or creatinin solution with the acid mercuric nitrate a dilute alkali was added, a white precipitate was readily formed.

It may also be mentioned that the specially valuable precipitant for creatinin, zinc chloride,* also gives precipitates—flocculent rather than crystalline—with both creatin and urea. These precipitates are moderate in amount, but gradually increase, so that separation from these substances must be effected before the precipitation of creatinin-zinc chloride can be made the basis for an accurate determination.

It seemed desirable to secure new determinations of the heat of combustion of creatin and creatinin, using a portion of the material prepared for these experiments. Such determinations were made, by the kindly offered aid of Prof. W. O. Atwater, in the chemical laboratory of the Storrs Connecticut Experiment Station, at Middletown, Conn., with the improved form of bomb-calorimeter. The specimens of air-dried creatin and creatinin were dried in air for five hours at 96°, and gave, for water-free substance, creatin 88.88 per cent and 88.075 per cent, and creatinin 93.66 per cent and 93.70 per cent.

These dried samples were burned, and yielded results as below. They kindled with great difficulty, not even naphthalene serving to ignite them. The substance was finally burned by inclosing in a gelatin capsule of known weight and making allowance for the heat of combustion

* Bulletin, No. 66, United States Department of Agriculture, Office of Experiment Stations.

* The investigations of the author confirm the statement of Schäfer ("Physiology," p. 100), that unless the proper conditions be exactly observed the precipitation of creatinin with zinc chloride is very uncertain and unsatisfactory.

of the capsule. The heats of combustion of 1 grm. of water-free substance were, in large calories,—

	Calories.
Creatin, first combustion	4'269
Creatin, second combustion	4'264
Average.. .. .	4'267
Creatinin, first combustion	4'578
Creatinin, second combustion	4'588
Average.. .. .	4'583

From these results we have, as the value for the molecular heat of combustion:—Creatin, 559 calories; creatinin, 517.9 calories; and the conversion in the human body of each molecule counted in grms.) of creatin into creatinin involves heat consumption to the extent of 41.1 calories.

Method Devised and Employed for Separation of Creatin, Creatinin, and Urea in Urine.

Before stating the method worked out and adopted for the quantitative determination of the three substances, creatin, creatinin, and urea, in urine containing the usual normal constituents, it may be well to note the character and strength of the reagent solutions used. It was desirable to have these in a fairly concentrated form, so as to reduce as much as possible the volume of liquid to be evaporated, and thus diminish the chance of creatin becoming converted into creatinin, or the reverse.

The reagents were as follows;—

1. Milk of lime, a thin fluid pulp of pure calcium hydroxide, for the most part in suspension, in water.
2. Aqueous solution of pure neutral calcium nitrate (200 grms. to the litre). The object of using nitrate rather than chloride for the removal of phosphates, &c., was to avoid the addition of large quantities of mercuric nitrate, which would otherwise have been necessary before urea could be precipitated. A calcium rather than a barium salt was used, notwithstanding the consequent failure properly to remove sulphates. The calcium nitrate, added as such, as well as that subsequently formed in the liquid under treatment, is easily soluble in alcohol, while barium nitrate is not.
3. Dilute nitric acid; 100 grms. acid per litre of water.
4. Aqueous solution of mercuric nitrate; 300 grms. to the litre, with just enough free nitric acid to render the solution clear and prevent formation of a basic salt.
5. Alcoholic solution of zinc chloride; a nearly saturated solution in 90 per cent alcohol.
6. Alcoholic solution of sodium acetate; a saturated solution in 90 per cent alcohol.
7. Acetic acid; about 40 per cent.
8. Sodium hypobromite, prepared by mixing equal volumes of an aqueous solution of sodium hydroxide (340 grms. to the litre) and one of bromine (200 grms.) and potassium bromide (240 grms.) per litre.

To the portion of urine to be treated—usually about 250 or 300 c.c.—there was added, with constant stirring, milk of lime until the reaction was distinctly alkaline and 20 c.c. of the solution of calcium nitrate. After standing for an hour the turbid liquid was filtered, drained with the aid of a filter-pump, and washed once or twice with a small amount of water. The filtrate was tested with a drop or two of the calcium nitrate solution in order to make sure that precipitation of phosphates, &c., was complete. It was then accurately neutralised with a few drops of dilute nitric acid, and urea was precipitated with the solution of mercuric nitrate, avoiding any large excess of the reagent. As soon as the flocculent precipitate had settled, and before it had time to become crystalline and granular, it was filtered off with a filter-pump and washed sparingly with water. The filtrate was tested to make sure that the precipitation of urea was complete.

This precipitate was washed off from the filter into a

beaker (owing to its bulkiness more than one filter had sometimes to be used), well stirred up with water, and decomposed by a rapid stream of sulphuretted hydrogen gas. The gas was passed through the liquid long enough to insure complete conversion of all the mercury into sulphide. The mercuric sulphide was removed by filtering, the filtrate evaporated to dryness at a gentle heat over a water-bath, and the residual urea nitrate weighed, a check upon its amount being obtained by re-dissolving it, and from an aliquot part determining the nitrogen evolved by means of sodium hypobromite, adding pure potassium cyanate and introducing the bromine solution separately after the caustic soda, as recommended by Allen. This precipitation of urea by mercuric nitrate in acid solution is not complete, but it largely reduces the amount to be separated from the flesh bases. In some experiments urea was not determined, and in some of these the precipitation with mercuric nitrate was omitted. In view of the observation of Meissner that the solubility of creatin in alcohol is increased by the presence of urea, it is better to remove the bulk of the urea in every case.

Through the liquid filtered off from the precipitate produced by mercuric nitrate a stream of sulphuretted hydrogen was passed as long as it gave rise to any precipitate, and mercuric sulphide was removed by filtration. The filtrate was *very accurately* neutralised by milk of lime, and evaporated at a temperature not exceeding 40°C. in a partial vacuum produced by a good filter-pump. When the volume had been reduced to about 5 c.c. alcohol of 90 per cent was added in such quantity as would little more than suffice to hold in solution the quantity of creatinin supposed to be present. A little absolute alcohol was used to make, with the small quantity of water remaining unevaporated, a uniform strength for the whole of 90 per cent. The alcoholic liquid was allowed to stand for three or four hours, being occasionally stirred, and was then filtered.

The residue left upon the filter, having been lightly washed with 90 per cent alcohol, was treated with a small amount of boiling water and again filtered. The undissolved matter on the filter, consisting mainly of crystalline calcium sulphate, was washed twice with small quantities of boiling water. The aqueous filtrate was evaporated to dryness over a water-bath, and the residue, creatin, was dried at 100°C. and weighed. The creatin was not absolutely pure, still retaining a little calcium sulphate and some organic compound of calcium which left lime on being strongly ignited. The creatin was re-dissolved and re-crystallised, the microscopic appearance of the crystals was observed, and two or three tests for the identity of the substance applied (silver nitrate and potash, picric acid, &c.).

The alcoholic solution filtered off from the creatin, &c., was concentrated by evaporation to about one-fifth of its original volume; a little of the alcoholic solution of sodium acetate was added, with enough acetic acid to produce slightly acid reaction. The creatinin was then precipitated by the addition of alcoholic solution of zinc chloride, allowing the liquid to stand in a well-covered vessel for three or four days before filtering. The creatinin-zinc chloride was washed on a dried filter with a moderate amount of 90 per cent alcohol, dried at 100°C., and weighed. The whole volume of alcohol, including the washings, was noted and a correction applied for the small amount of creatinin-zinc chloride retained in it in solution. After weighing, the precipitate was carefully examined with a microscope to see that it was free from sodium chloride or other visible impurities, and in two or three instances its identity was still further established by determinations of zinc and chlorine.

Having ascertained that the precipitation of creatinin by zinc chloride was complete, a determination of such urea as remained in the filtrate was made with an aliquot part of it by means of sodium hypobromite, and the result added to that from the urea previously recovered as nitrate.

In carrying out this process there was found to be considerable advantage in using of each reagent—*e.g.*, mercuric nitrate and zinc chloride—an amount calculated on the basis of approximate knowledge of the quantities present of the substances to be determined, such as to provide for a very small surplus only of the reagent, always, however, testing afterwards to make sure that enough had been employed.

Before proceeding to the physiological work a number of experiments were made to ascertain how far the analytical method might be trusted. Known amounts of creatin, creatinin, and urea were added to a portion of normal urine. Comparative determinations of these three substances were then made. Similar determinations were also made in another sample of the same urine which had not received such additions. Neglecting three or four preliminary experiments, in which the method was being worked out and in which the procedure was not uniform, the results given below were obtained. In each case the urine employed was the mixed total excretion of twenty-four hours. Of this two samples were taken, each one-fifth of the whole. To facilitate comparison with other results recorded later, the figures actually obtained have been multiplied by five, so that the report stands as for the whole daily quantity.

In the following table is shown the amount of urea, creatinin, and creatin found in nine samples of the total normal urine excreted in twenty-four hours:—

Constituents of Normal Urine.

Number of sample.	Urea. Grms.	Creatinin. Grm.	Creatin. Grms.
1	29.246	0.781	—
2	29.092	0.832	—
3	28.608	0.894	—
4	30.125	0.695	—
5	28.538	0.753	—
6	28.866	0.844	—
7	27.764	0.869	—
8	28.933	0.815	—
9	29.122	0.872	—

In the following table is shown the amount of urea, creatinin, and creatin added to ten samples of the same urine mentioned above, together with the amount and percentage of added material recovered.

Materials Added to Urine and Amounts Recovered.

Number of sample.	Additions made to urine.			Added materials recovered.*					
	Urea. Grms.	Creatinin. Grms.	Creatin. Grms.	Urea. Grms.	Creatinin. Grms.	Creatin. Grms.	Urea. Per cent.	Creatinin. Per cent.	Creatin. Per cent.
1.	2	1	—	1.948	0.956	—	97.4	95.6	—
2.	2	1	—	1.941	0.948	—	97.0	94.8	—
3.	3	2	—	2.895	1.898	—	96.5	94.9	—
4.	5	3	1	4.846	2.856	0.863	96.9	95.2	86.3
5.	5	4	1	4.721	3.903	0.845	94.4	97.6	84.5
6.	7	5	1	6.811	4.776	0.856	97.3	95.5	85.6
7.	8	5	2	7.736	4.635	1.769	96.7	92.7	88.4
8.	8	8	2	7.592	7.609	1.774	94.9	95.1	88.7
9.	10	10	3	9.683	9.392	2.635	96.8	93.9	87.8
Average							96.4	95.0	86.9

* After deducting from the amounts actually found those due to the normal constituents.

Although the process used is less favourable to the accurate determination of creatin than to that of creatinin, it may well be suspected that the difference between the two is not quite so great as seems to be shown by these figures, it being quite conceivable that, in spite of the precautions taken, some little conversion of creatin into creatinin may have occurred under the treatment applied. This would of course tend to raise the results obtained for the latter substance and to lower those of the former.

(To be continued).

THE ESTIMATION OF OXYGEN IN COAL-GAS.

By Dr. H. LUBBERGER.

THE estimation of the oxygen contained in coal-gas is not an easy operation, as it constitutes hardly 0.2 or 0.3 per cent of the total volume; that is to say, with the ordinary gasometric apparatus we have to measure 0.2 to 0.3 c.c. of gas. It is, however, important to have a method enabling us to estimate exactly the oxygen in ordinary coal-gas, considering that it is more and more recognised that a small addition of air to the raw gas helps the purification very considerably.

It is evident that as the apparatus of Bunte or of Hempel do not allow of a volumetric determination, we might perhaps make use of Rüdorff's apparatus. With a receiver of 1 litre capacity each per cent of oxygen would be represented by a diminution of volume of 1 c.c. But the readings would be false, inasmuch as other gases accompany coal-gas, as well as oxygen, and they would be absorbed in quantities too great to overlook.

The process lately described by Dr. Pfeiffer (*Fourn. f. Gasbeleuchtung*, 1897, p. 356), for estimating the proportion of oxygen contained in coal-gas, necessitates the use of an empirical solution of caramel, which would certainly not remain unchanged for years, which is a serious inconvenience.

I have attempted to modify E. W. Winkler's process (*Berichte*, 1888, xxi., II., 2843), in such a manner as to make it applicable with Bunte's burette.

This process depends on the oxidation, by means of the oxygen dissolved in water, of an alkaline solution of manganous hydroxide to the state of manganic hydroxide. By adding potassic iodide and hydrochloric acid, a quantity of iodine is set free equal to the amount of oxygen dissolved, and it is only necessary to titrate with a solution of hyposulphite to estimate the quantity of oxygen present.

The following are the reagents necessary:—

1. A solution of potassic iodide; 10 grms. of caustic soda, 15 grms. of crystallised Seignette salts, and 8.5 grms. of potassic iodide are dissolved in 300 c.c. of water.
2. A manganous solution; 14.5 grms. of manganous sulphate ($\text{MnSO}_4 + 5\text{H}_2\text{O}$) in 100 c.c. of water.
3. A centinormal solution of hyposulphite of soda;

2.48 grms. of hyposulphite ($\text{Na}_2\text{S}_2\text{O}_3 + 5\text{H}_2\text{O}$) dissolved in 1 litre of water.

It is further necessary to have water free from air prepared by Pfeiffer's method (*Fourn. f. Gasbeleuchtung und Wasserversorgung*, 1897, p. 356).

To introduce the gas to be analysed into the burette, the latter is filled with water, and the gas passed in through the upper tap. The lower tap is then closed, and the upper one turned through an angle of 180° .

During this operation the gas being in the burette

under pressure drives the air out from the passage through the tap. The tube through which the gas is passed is then removed, and the outer side of the tap is covered with a short piece of indiarubber tube plugged with a bit of glass rod. About 5 c.c. of water free from air are poured in through the funnel, and allowed to run into the burette in such quantity that it forms a layer of about 1 c.c. above the lower tap. The lower tap is then carefully opened, and enough water allowed to run out to fill the capillary tube which is above and below the tap.

This method of working applies to the case of a sample of gas taken from a pipe where it is under pressure, but when the gas has to be pumped from the pipe it is necessary to fill the taps with water at first to prevent any air entering the burette during the subsequent treatment. The burette thus filled is fixed on its support, and water free from air is passed in through the upper end, up to the third degree above zero, and the excess of gas is allowed to escape through the three-way tap, the funnel being full. After reading the level the water is run off down to the tap and the funnel emptied.

The further treatment of the gas varies according to whether the sample of gas was taken before or after passing through the purifiers; that is to say, according to whether it contained sulphuretted hydrogen or not.

I. Gas taken after Purification—that is to say, Free from Sulphuretted Hydrogen.—One c.c. of manganous solution is passed in by the upper tap, and then 30 c.c. of potassic iodide solution by the lower tap. The burette is then well shaken in such a manner that the liquid contained in it passes up and down the whole length of the burette at each shake. This operation is continued for ten minutes; after this, 1 c.c. of concentrated hydrochloric acid (at 25 per cent) is passed in through the lower end, and the whole turned over. In the case of a gas containing oxygen, iodine is set at liberty. The funnel is then filled with ordinary distilled water, and the contents of the burette are then transferred to a beaker. We then add a little 1 per cent starch, and titrate with centinormal hyposulphite of soda until the blue colour disappears. It is necessary to subtract 0.3 c.c. from the volume of hyposulphite used, and the proportion of oxygen present is then calculated, each 1 c.c. of hyposulphite being equivalent to 0.06 c.c. of oxygen; that is to say, 0.06 per cent by volume when we take 100 c.c. of gas. We can perform the whole operation in the same burette, but in this case the correction to be made would be 0.06 c.c.

II. Gas taken before Purification—that is to say, containing Sulphuretted Hydrogen.—As sulphuretted hydrogen interferes with the operation, and is not without action on the reagents employed, it should be previously removed. After running off the water 2 c.c. of iodine solution (5 grms. of iodine and 10 grms. of potassic iodide in 100 c.c. of water) are passed into the burette by the lower tap, and shaken vigorously several times.

The solution of iodine is run off, and the last traces removed by washing with the smallest possible quantity of water free from air, introduced by the upper tap. The last washings should be without action on starch. Continue the operation as in the first case.

Analysis gives the following results:—

Oxygen added. C.c.	Oxygen found. C.c.	Oxygen added. C.c.	Oxygen found. C.c.
0.104	0.099	0.313	0.297
0.104	0.111	0.418	0.427
0.209	0.204	0.418	0.409
0.209	0.186	0.627	0.657
0.209	0.210		

The small differences arise from the fact that we take 1.0 c.c. of hyposulphite as being equivalent to 0.06 c.c. of oxygen, without allowing for temperature and pressure. But as this is purely a commercial method such small differences may be neglected.—*Fourn. f. Gasbeleucht. und Wasserversorg.*, xii., p. 695.

ON A TEST,
BY THE FREEZING-POINT METHOD,
OF THE
IONISATION COEFFICIENTS DETERMINED BY
THE CONDUCTIVITY METHOD,
FOR
SOLUTIONS CONTAINING POTASSIUM AND
SODIUM SULPHATES.*

By E. H. ARCHIBALD, M.Sc.,
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(Continued from p. 47).

Determination of Equivalent Conductivity at Infinite Dilution for 0° C.

For this purpose a series of simple solutions of each electrolyte, of concentrations ranging from 0.01 to 0.0001 gm.-equivalents per litre, were prepared, and their conductivities were measured both at 18° C. and at 0° C. The conductivity of the water used in their preparation was also measured at both temperatures and subtracted in each case from the conductivity of the solutions. Table I. gives the results of the observations, together with the values of the temperature coefficients, $(\mu_{18} - \mu_0)/\mu_{18}$. Concentrations are expressed in gm.-equivalents of anhydrous salt per litre and conductivities in terms of 10^{-8} times the conductivity of mercury at 0° C. The conductivities at 18° were tested by comparison with Kohlrausch's values; these values, when plotted on co-ordinate paper, being found to lie practically on the same curve as mine.

It will be seen that the temperature coefficients for potassium sulphate solutions diminish with increase of dilution while those for sodium sulphate increase. This result† was so unexpected that I thought it well to repeat the observations, the result being substantiated by the repetition.

It will be seen, also, that in both cases the coefficients reach constant values as concentration is diminished; in the case of $\frac{1}{2}\text{K}_2\text{SO}_4$ from a concentration of 0.0004 on, in that of $\frac{1}{2}\text{Na}_2\text{SO}_4$ from 0.0006 on. Assuming, then, that these values will hold for infinite dilution, the equivalent conductivities at infinite dilution for 0° C. may be determined from Kohlrausch's values (*Wied. Ann.*, 1893, l., 406) for 18° C., viz., 1270×10^{-8} and 1070×10^{-8} for $\frac{1}{2}\text{K}_2\text{SO}_4$ and $\frac{1}{2}\text{Na}_2\text{SO}_4$ respectively. They were found thus to have the values 800×10^{-8} and 646×10^{-8} respectively, expressed in terms of the conductivity of mercury at 0° C.

Determination of the Ionisation Coefficients of Simple Solutions.

Both for the purpose of finding how closely the lowering of the freezing-point could be calculated for simple solutions and for the purpose of determining the ionisation coefficients of the electrolytes in the mixtures, it was necessary to know the ionisation coefficients of a sufficiently extended series of simple solutions of the two electrolytes. Table II. contains the observations of conductivity made for this purpose, together with the values of the ionisation coefficients calculated on the assumption that for simple solutions they are equal to the ratios of the equivalent conductivity to the equivalent conductivity at infinite dilution. The table gives also the ionisation coefficients at 18° C. obtained from the conductivity observations of former papers (*Trans. N.S. Inst. Sci.*, 1897-8, ix., 291 and 307). These quantities are not needed for the present purpose. But the knowledge of the ionisation coefficients at 0° enables us to determine how, in the case of the electrolytes under consideration, the state of ionisation in

* From the *Transactions of the Nova Scotian Institute of Science*, vol. x., Session 1898-99.

† The results of this table are in close agreement with those obtained by Deguisne ("Dissertation," Strassburg, 1895), of which Mr. Archibald was not aware.—J. G. M.

TABLE I.

Potassium Sulphate Solutions.				Sodium Sulphate Solutions.			
Concentration at 18° C.	Equivalent conductivity (μ).		$(\mu_{18} - \mu_0)/\mu_{18}$	Concentration at 18° C.	Equivalent conductivity (μ).		$(\mu_{18} - \mu_0)/\mu_{18}$
	At 18° C.	At 0° C.			At 18° C.	At 0° C.	
0.010	1099	687	0.375	0.010	907	555	0.388
0.008	1116	698	0.375	0.008	919	562	0.389
0.005	1142	716	0.373	0.005	946	577	0.390
0.004	1155	723	0.374	—	—	—	—
0.002	1180	740	0.373	0.002	981	596	0.393
0.001	1206	757	0.372	0.001	997	604	0.394
0.0008	1213	762	0.372	0.0008	1003	607	0.395
0.0006	1221	768	0.371	0.0006	1008	609	0.396
0.0005	1225	771	0.371	0.0005	1012	611	0.396
0.0004	1230	775	0.370	—	—	—	—
0.0002	1240	781	0.370	0.0002	1027	620	0.396
0.0001	1248	786	0.370	0.0001	1036	626	0.396

simple solutions varies with the temperature. Concentrations and conductivities are expressed in terms of the same units as in Table I.

TABLE II.

Concentration at 18° C.	Equivalent conductivity at 0° C.		Ionisation coefficients.			
			K_2SO_4 .		Na_2SO_4 .	
	$\frac{1}{2}K_2SO_4$.	$\frac{1}{2}Na_2SO_4$.	At 18° C.	At 0° C.	At 18° C.	At 0° C.
0.050	604.2	486.0	0.757	0.755	0.733	0.752
0.055	598.0	480.0	0.750	0.748	0.728	0.743
0.060	594.1	475.5	0.745	0.743	0.723	0.736
0.070	585.4	466.5	0.736	0.732	0.715	0.722
0.080	577.5	460.0	0.723	0.722	0.703	0.712
0.100	564.0	448.5	0.706	0.705	0.686	0.694
0.125	547.5	434.0	—	0.684	—	0.672
0.150	535.0	422.5	—	0.669	—	0.654
0.200	516.0	403.1	0.650	0.645	0.601	0.624
0.250	503.0	387.4	0.634	0.629	0.586	0.600
0.300	493.0	373.5	0.620	0.616	0.570	0.578
0.350	485.0	362.4	0.605	0.606	0.556	0.561
0.400	478.0	353.0	0.595	0.598	0.545	0.546
0.450	473.0	345.5	0.587	0.591	0.533	0.535
0.500	470.0	339.6	0.580	0.588	0.522	0.525
0.600	466.0	330.0	0.567	0.583	0.506	0.511
0.700	464.0	324.2	0.551	0.580	0.498	0.501

It appears from these results that in the case of solutions of potassium sulphate the ionisation coefficient increases very slightly with rise of temperature between 0° and 18° C. from a concentration of 0.05 to one of about 0.35, and that from this concentration to one of at least 0.7 it decreases, the magnitude of the decrement increasing rapidly with the concentration, and amounting at a concentration of 0.7 to 5 per cent. In the case of sodium sulphate, the coefficient diminishes with rise of temperature throughout the whole range of concentration observed, the amount of the decrement diminishing with increase of concentration, until at a concentration of 0.7 it is only 0.6 per cent.

Method of Measuring Depression of the Freezing-point.

Of the different methods described for the determination of the freezing-point of salt solutions, that of Loomis (*Phys. Review*, 1893, i., 199 and 274; 1896, iii., 270) appeared to me the best, and to give the most concordant results. His method was accordingly followed in making the measurements below.

As it is most essential that the temperature of the room where the observations are made should be near zero and as constant as possible, the measurements were carried out during the winter months in a basement room of Dalhousie College building, where it was found possible to keep the temperature below 2° C. and constant to within 0.5 of a degree for a couple of hours at a time. No measurements were made while the temperature of the room was above 2° C.

The thermometer was of the ordinary Beckman form, graduated to 0.01 of a degree. No reading microscope being available, I had to be satisfied with the use of an ordinary hand lens for this purpose. Nevertheless, as the divisions of the scale were about 0.6 m.m. in length, I am quite satisfied that I was able to read the temperatures to at least 0.001 degree. The following readings of the thermometer made in an experiment for determining the freezing-point of water would seem to imply that I succeeded in reading even more closely:—2.3415, 2.3410, 2.3420, 2.3415, 2.3420. Mean reading, 2.3416. Greatest divergence from mean, 0.0006.

The thermometer had never been calibrated, and as apparatus for this purpose was not available, I did not attempt to calibrate it myself. The length of scale used for the following measurements, however, was less than what corresponded to 1.4 degree, and for the more dilute solutions, say below 0.1 gm.-equivalent per litre, less than what corresponded to 0.2 of a degree.

The freezing and melting baths were each of earthenware, about 32 c.m. long and with an internal diameter of about 9 c.m. In the former was a mixture of snow and water with enough common salt added to keep the temperature at about -12° C. The latter contained a mixture of snow and water, the temperature of which was about 0.2° C.

The protection bath, which was of glass 35 c.m. deep and 8 c.m. in diameter, was provided with a covering of felt to minimise the effect of the surrounding air. It contained a mixture of snow and air with sufficient salt added to keep the temperature from 0.3° to 0.28° below the freezing-point of the solutions to be measured. After some experience had been gained, little trouble was found in keeping the temperature of this bath constant within a twentieth of a degree during several observations of any one solution.

The freezing tubes first tried were of the following dimensions:—The inner one 22 c.m. long with an external diameter of 2.4 c.m., the outer one 20 c.m. long with an internal diameter of 2.7 c.m., the thickness of the glass of both tubes being 1 m.m. There was thus an air space of about 1.5 m.m. between the tubes. This was found to be too great, as shown by its being difficult to prevent ice from forming around the bulb of the thermometer despite the most vigorous stirring. The next ones tried were as follows:—The inner tube was 28 c.m. long with an external diameter of 2.7 c.m., the outer tube 26 c.m. long with an internal diameter of 2.85 c.m., the thickness of the glass being the same as before. There was thus an air space of about 0.7 m.m. between the tubes. This was found to be hardly enough, as there was a tendency for the ice to form on the walls of the tube and thus cause much delay. As I worked with 75 c.c. of solution, the greater length of these tubes allowed the solution to be immersed well into the bath, rendering it almost free from the influence of the outside temperature. The inner tube was therefore retained and an outer tube provided of

about the same length and thickness of walls, but with an internal diameter of 2.88 c.m., thus leaving an air space of about 0.9 m.m. between the tubes. This gave complete satisfaction. With uniform stirring no tendency was observed for the ice to form on the walls of the tube or on the bulb of the thermometer, or to freeze in a mass. The inner tube had its lower end re-entrant, as recommended by Loomis.

I should like to draw attention to the importance of having the air space between the two tubes of the proper size. If the importance of this point has been noted by former observers it has escaped me.

The hammer used for tapping the thermometer was part of a small electric bell and was covered with a piece of thick rubber tubing. It was found to be very essential to drive the hammer so that the blows on the thermometer might be of uniform strength. Some difficulty was met with in attaining that end; but by careful attention to the strength of the current what appeared to be sufficient uniformity was attained.

The stirrer was of the ordinary ring form, the upright rod passing through a glass tube, the upper end of which was constricted, and the lower so far from the solution that the wetted portion of the stirrer could not touch it. A stop on the upright rod limited the extent of the stroke so that the ring would not leave the solution, and ensured the equality of the strokes. It was worked by hand as uniformly as possible.

The over-cooling was seldom over 0.1° , owing doubtless to the low temperature of the room in which the observations were made. There was consequently no need of correcting for over-cooling.

The freezing-point of water was determined each day before determining that of the solutions, and in the event of any appreciable change occurring in the atmospheric pressure during the observations on the solutions, the observation on water was repeated.

(To be continued).

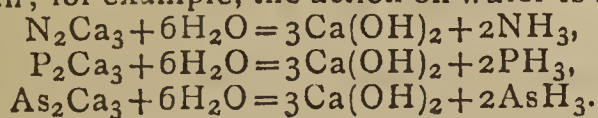
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 1, July 3, 1899.

Volumetric Estimation of Zinc.—M. Pouget.—The author estimates zinc volumetrically by the method employed by MM. Rollet and Campredon for the estimation of sulphur. The zinc solution is precipitated by sulphuretted hydrogen. To the sulphide of zinc thus obtained is added a known quantity of iodine solution; the excess of the latter being titrated with thiosulphate solution, $\text{ZnS} + 2\text{I} = \text{ZnI}_2 + \text{S}$. The reaction is complete at the end of a few minutes. This method, however, can only be really practical if the filtration and washing of the zinc sulphide is avoided, and this is accomplished by boiling off the excess of sulphuretted hydrogen instead of filtering the zinc sulphide.

Preparation and Properties of Arsenides of Strontium, Barium, and Lithium.—P. Lebeau.—The author prepares the arsenides of calcium, barium, and strontium by the reduction of the arseniates of the alkaline earths by means of carbon at the temperature of the electric furnace. These compounds resemble, in their formulæ and their properties, nitrides and the phosphides of this group which were prepared in a state of purity by M. Moissan; for example, the action on water is similar:—



Amongst the arsenides of the metals of the alkalis, lithium arsenide is the only one which is stable enough to be prepared by the electric furnace.

Oxymethylene-cyanacetate of Methyl and some of its Homologues.—E. Grégoire de Bollemont.—The author has already described the preparation of methylic, ethylic, and amylic oxymethylenecyanacetates from the corresponding ethereal salts. He now has studied the properties of these substances, and finds that all these compounds exhibit the characteristics of strong monobasic acids, and they may be regarded as substitution derivatives of formic acid.

Use of Tetrachlorhydroquinone for the Identification and Separation of the Fatty Acids.—L. Bouveault.—When tetrachlorhydroquinone reacts with either one or two molecules of the chlorides of the fatty acids, stable compounds are formed which are well crystallised and easily purified, and so can be used for the identification of the acids, and in some cases for the separation also. The author describes the physical properties of some of compounds thus formed.

Contribution to the Study of the Bark of Rhamnus purshiana.—M. Leprince.—The author has separated and identified chrysarobin, chrysophanic acid, and emodine in the bark of the above tree.

Direct Transformation of Acetamide into Ethylamine by Hydrogenation.—M. Guerbet.—This reduction is brought about by the action of metallic sodium in the presence of boiling amylic alcohol.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxi., No. 5.

Speed and Limit of Etherification of Phosphoric Acid by Methylic Alcohol.—G. Belougou.—As the result of a series of experiments the author concludes—1. That by reacting with anhydrous phosphoric acid on methylic alcohol the limit of etherification is attained immediately. This limit is independent of the conditions under which the mixture of alcohol and acid is made. 2. Heat and time retard the coefficient of etherification, which has a minimum of about 10 per cent. 3. The presence of a small quantity of water diminishes the value of this coefficient in a very remarkable manner.

Composition of the Osmiamates.—L. Brizard.—Already inserted.

Complex Salts of Palladium: Palladoxalates.—M. Vèzes.—Already inserted.

Two New Organic Acids derived from Cyano-succinate of Ethyl.—L. Barthe.—Two ethers are formed by acting with bromide of trimethylene on cyanosuccinate of ethyl soda. One, which is well crystallised, is saponified, and gives rise to a substance answering to the formula $\text{C}_{11}\text{H}_{16}\text{O}_8$; it melts at $159-160^{\circ}$, is very soluble in water, and fairly so in acetic acid, from which it eventually separates by crystallisation. The other ether, which is liquid, is treated with hydrochloric acid, and the crystalline mass obtained (which contains chlorhydrate of ammonia), together with the acid which has been formed, are treated with anhydrous ether. This solution, submitted to evaporation, leaves a crystalline residue, which is easily purified by a further crystallisation. This acid melts at $143-144^{\circ}$, is soluble in ether, alcohol, acetic acid, and water; it corresponds to the formula $\text{C}_8\text{H}_{12}\text{O}_6$ and is tribasic.

On the Chlorobromophenes.—V. Thomas.—In this paper the author describes some new compounds which he has obtained in a fairly pure state; and also describes the general method of the preparation of the chlorobromides, $\text{C}_6\text{H}_{(5-n)}\text{BrCl}_n$. The method consists of heating together in a flask with a reflux condenser bromide of phenyl and ferric chloride. The proportions to be used are very variable. The reactions begin at a

low temperature (about 40°) and proceed slowly. By increasing the temperature hydrochloric acid is given off in abundance, and if raised to the sublimation point of ferric chloride, the fumes are immediately reduced and ferrous chloride formed. At a high temperature, the derivatives rich in chlorine have a greater tendency to form; for it is a general fact in the whole series, that the more a compound is chlorised, the more difficult the final chlorination becomes, and thus requires more heat.

The Constitution of the Colouring-matters of the Safranin Series.—G. F. Jaubert.—The object of this paper is to answer the questions:—1. Have the safranins a symmetric constitution? 2. In the salts of safranin, such as the chlorhydrates, where is the salifiable group containing the Cl radical to be found—fixed to the azinic nitrogen, or fixed to the diazotable NH_2 radical? The author is able to reply in the affirmative to the first of these two questions; and to the second—that is, the position of the salifiable group—numerous considerations have led him to adopt the paraquinoid formula (that is, the latter one) for the red monodiazotable salts used in the arts under the name of safranin, but he reserves to himself the right to return to this important point in a future research.

Extraction and Synthesis of the Odorous Principle of Jasmine Flowers.—A. Verley.—Already noticed.

Triacetylmorphine and the Oxidation of Morphine.—H. Causse.—Already noticed.

Anabsinthine.—M. M. Adrian and Trillat.—The authors describe the principal methods known for the production of absinth, and show how they differ from their own, by which they obtain anabsinthine. The principal points of difference in the two products are the following:—

	Absinthine.	Anabsinthine.
Fusing-point	68°	258—260°
Composition	$\text{C}_{15}\text{H}_{20}\text{O}_4$	$\text{C}_{18}\text{H}_{24}\text{O}_4$

A Crystallised Fibrine.—L. Maillard.—The contents of some antidiphtheritic toxine tubes were noticed after about three months to have become turbid and contain a very dense pulverulent deposit; this on examination proved to be fibrine in microscopic crystals.

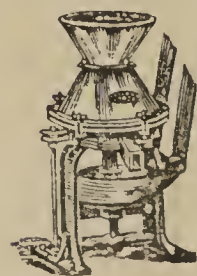
New Method for the Detection and Estimation of Acetone in Water and in Methylic and Ethylic Alcohols.—G. Denigès.—Already noticed.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Petroleum and its Products.—Will any reader kindly give the name or address of any institution in or around London where classes are held dealing with the chemistry of Petroleum and its Products.—C. H.

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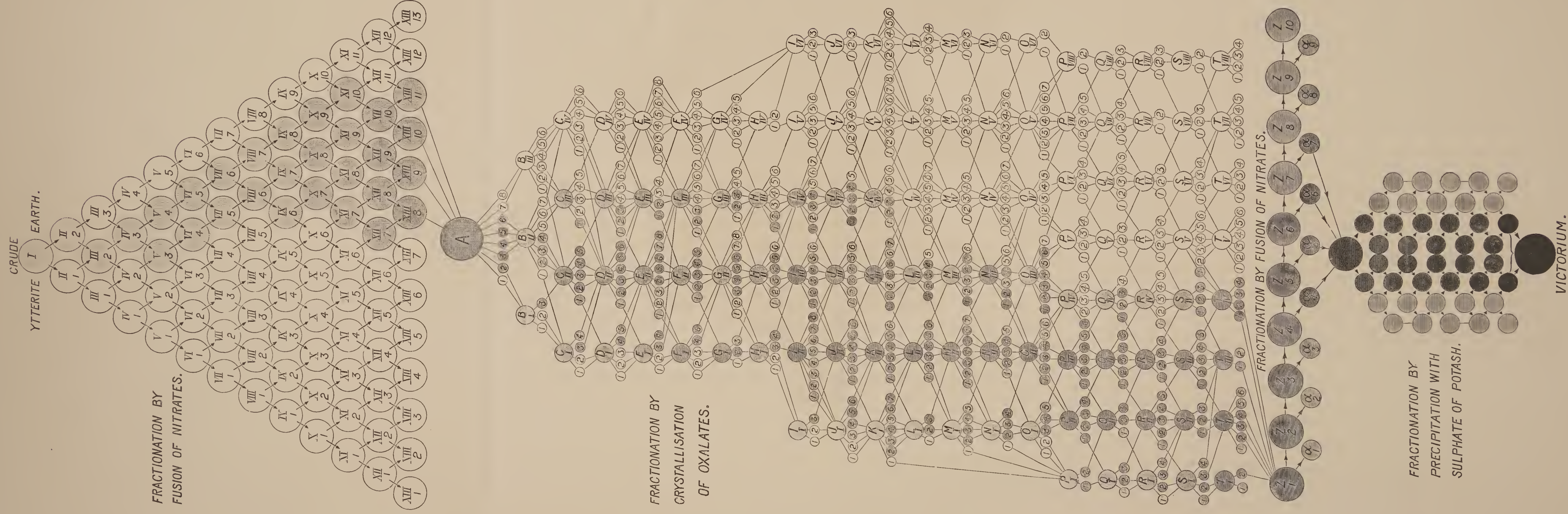
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THE CHEMICAL NEWS.

VOL. LXXX, No. 2072.

ON THE WATERS OF THE SALT LAKE OF URMI.*

By R. T. GÜNTHER, M.A.,

and

J. J. MANLEY, Daubeney Curator, Magdalen College.

IN June, 1897, a portion of the Government Grant was allotted to one of the authors by the Committee of the Royal Society, for the investigation of the fauna and flora of the great salt lake of Urmi, in Persia, as well as of the relations of that fauna and flora to its environment. The present research was undertaken with the view of placing on record some of the conditions prevailing in the lake at the present day.

The extraordinary changes which the level of the waters of the lake has undergone, and is still undergoing, enhance the importance of periodical examinations of the nature of the waters. The advisability of the preservation of such records was urged upon the Royal Society by its Secretary, 184 years ago. Edmund Halley, in his "Short Account of the Cause of the Saltiness of the Ocean, and of the Several Lakes that emit no Rivers," expressed himself as follows:—"I recommend it therefore to the Society, as opportunity shall offer, to procure the Experiments to be made of the present degree of Saltiness of the Ocean, and of as many of these Lakes as can be come at, that they may stand upon Record for the benefit of future Ages" (*Phil. Trans.*, 1715, vol. xxix., p. 299). At the present day there are additional reasons for recording the properties and composition of such salt lakes as are known to be inhabited by life, because Schmanke-witsch (*Zeitschrift Wiss. Zoologie*, 1875, vol., xxv.), and many others of the modern school of *Entwickelungsme- chanik* (Morgan, Loeb, Vernon, &c.), have proved that every change in the salinity of the waters is accompanied by definite, rapid, and corresponding changes in the anatomical structure of certain of their halophilous fauna, and especially in the species of *Artemia*, one of which occurs in Lake Urmi (Günther, *Nature*, vol. lviii., p. 435).

The superficial area covered by Lake Urmi is about 800 square miles, or about twice that of the Dead Sea. For so large an expanse of water its depth is inconsiderable; the greatest soundings do not exceed 40 feet, and since much of the lake is extremely shallow, its average depth is probably under 20 feet. When viewed from the commanding heights of one of its islands, its waters show that brilliant deep blue colour which is so characteristic of salt lakes, but as seen from a boat, the light which is reflected from the light grey mud at the bottom is green.

The temperature of so small a volume of water, which is at the same time so extended as Lake Urmi, must necessarily vary considerably with the seasonable changes of temperature. During the months of July and August the temperature of the surface waters varies from 27.8° C. to 25.8° C., and the temperature of the bottom water at a depth of about 25 feet was 25° C. The specific gravity of the water, as measured on the spot by an ordinary hydrometer, was 1.11, whether the water was drawn from near the bottom or from the surface of the lake; it may therefore be assumed that the waters of the lake remote from the mouths of the fresh water tributaries were of a fairly uniform density, a result which was probably due to the thorough mixing of the waters produced by the strong south-easterly breezes prevalent at the time.

The total quantity of water available for the more detailed examination was brought home in two glass wine bottles, holding about $\frac{3}{4}$ litre a-piece. The samples A and B were collected on September 16, 1898, near the base of the Bezau Daghi, on the western shore of the lake, where there is comparatively deep and clear water close in shore. The bottles were carefully corked, and it is, I think, fair to assume that no great changes have occurred in the interval between the bottling of the samples in Persia and their examination in Magdalen College Laboratory, in Oxford, seeing that the discrepancies between the analyses are very small.

The examination was both physical and chemical.

PHYSICAL EXAMINATION.

Determination of Specific Gravity.

The specific gravities of the two samples of water (A and B) were determined by Mr. H. N. Dickson, according to the method of Sprengel, with the following mean results:—

	A.	B.
Specific gravity, at 15° C. ..	1.11338	1.11389
" " " 0.3° C. ..	1.11891	1.11945
Difference	0.00553	0.00556

Determination of Refractive Index.

The refractive indices (μ) were determined by means of a hollow quartz prism of 60° 6' refracting angle, and a large spectrometer* reading to 2" of arc. The water was at a temperature of 12.2° C. during the readings.

	A.	B.
Angle of minimum deviation		
of D line	25° 50' 4"	25° 50' 35"
whence $\mu =$	1.36110	1.36122

It is believed that similar optical measurements will be found to be applicable to ordinary sea waters and will be found to give a more accurate and a more readily obtained indication of the physical nature of the water than the ordinary specific gravity methods.

Determination of Boiling-point.

It has long been customary to record the boiling-points of strongly saline natural waters, but in only too many cases, owing to the lack of description of the conditions of the experiment, the records have only a small value. Many trials have convinced us that the boiling-points of brines properly determined under similar conditions yield as reliable, although less minute, information concerning the degree of salinity as specific gravity determinations.

The salt water was boiled in a platinum bottle, to which an inverted condenser containing ice-cold water was attached, in order to prevent loss of water vapour and consequent concentration. The temperature was measured by a form of platinum resistance thermometer, which reads to 0.01° C. Three readings were always taken. Firstly, the temperature of the steam from ordinary boiling water in a steam jacket and under atmospheric pressure; secondly, the temperature of the boiling salt water; and finally, the temperature of steam once more. If the first and last readings were identical, it was considered that the conditions of the experiment had remained constant. As a matter of practice it was found that when once the boiling-point of the salt water had been reached, the water continued to boil at that temperature for any length of time, so long as the pressure remained constant.

	A.	B.
Boiling-point under normal		
pressure	103.84° C.	103.88° C.

It will thus be seen that the three results of the physical examination of the two samples A and B are all mutually confirmatory, in so far that they indicate that

* A Paper read before the Royal Society, June 15, 1899.

* The spectrometer which was constructed for Dr. Bedson, and the prism employed are the property of the Royal Society.

sample B had become a little more concentrated than A during its journey from Persia to Oxford.

CHEMICAL EXAMINATION.

The method adopted was that of Dittmar, as described in the "Report on the Composition of Ocean Water" ("Challenger Reports," *Physics and Chemistry*, vol i.).

For the estimation of the lime and magnesia, 20 c.c. of the water, weighing approximately 22.2 grms., were measured off, and the quantities used in the determination of the potash and total salts were half that amount.

Examination of the Correctness of Dittmar's Factor 0.91 for "Crude" Lime.

Forty c.c. of the water were measured off and weighed. In accordance with Dittmar's recommendation, the calcium was precipitated as oxalate, filtered, washed, and finally weighed as oxide. The "crude" oxide obtained amounted to 0.0319 gm. : this was then re-dissolved, and again precipitated and weighed as "pure" oxide; the weight was found to be 0.0284 gm. If we multiply the weight of crude lime, 0.0319 gm., by Dittmar's factor 0.91, we obtain 0.0290 gm. as the weight of "pure" lime. This amount only differs from that actually found by +0.0006 gm., thus affording confirmatory evidence of the correctness of the factor.

The quantities of pure lime given below were determined by re-precipitation and re-purification. The magnesia was precipitated by sodium phosphate instead of by ammonium phosphate as Dittmar recommends, because when the latter reagent was used the magnesia was found to come down very slowly, and to adhere inconveniently to the sides of the vessel.

The soda was determined by the method in which all the bases are converted into normal sulphates, and the weight of the mixed sulphates is diminished by the subtraction of the weights of the potassium, calcium, and magnesium sulphates. The potash was determined by precipitation from the mixed sulphates by chloride of platinum, according to Dittmar's third and final method ("Challenger Reports," *loc. cit.*, p. 16), and his observations upon the appreciable solubility of the finely divided platinum by the cold dilute hydrochloric acid employed for washing were confirmed.

From the known amounts of lime, magnesia, and potash (see below), were deduced the following weights of normal sulphates in 100 grms. of the mixed sulphates:—

	A. Grms.	B. Grms.
Potassium sulphate	0.258	0.259
Calcium sulphate	0.146	0.171
Magnesium sulphate	1.870	1.871
Sodium sulphate (by difference)	15.547	15.606
Total sulphates	17.821	17.907

The quantities of the principal saline components dissolved in 100 grms. of the water of Lake Urmi are—

	A.	B.
Lime (CaO)	0.0603	0.0706
Magnesia (MgO)	0.6265	0.6266
Potash (K ₂ O)	0.1394	0.1402
Soda (Na ₂ O)	6.788	6.814
Chlorine (Cl)	8.496	8.536
Sulphates (SO ₃)	0.6205	0.6312
	16.7307	16.8186
Oxygen equivalents of the chlorine to be deducted ..	1.9167	1.9258
Total salts in 100 grms. of water	14.814	14.893

Or, recalculated for 100 parts by weight of total salts, we have—

	A.	B.
Chlorine (Cl)	57.351	57.315
Sulphates (SO ₃)	4.189	4.238
Lime (CaO)	0.407	0.474
Magnesia (MgO)	4.229	4.207
Potash (K ₂ O)	0.941	0.941
Soda (Na ₂ O)	45.822	45.753
Deduct [O] per [Cl ₂]	-12.939	-12.931
	100.000	99.997

The hypothetical proximate composition of 100 parts of the total salts was calculated, with the following results:—

	A.	B.	
		i.	ii.
Sodium chloride	86.332	86.203	86.203
Magnesium chloride	6.661	6.816	6.816
" sulphate	4.211	4.150	3.915
Calcium sulphate	0.988	1.151	1.151
Potassium sulphate	1.741	1.741	1.741
	99.933	100.061	99.826

Result B i. was obtained by calculating the magnesium sulphate from the residual sulphate (SO₃). Result B ii. from the residual magnesium.

It is a remarkable fact that, notwithstanding the occurrence of limestone rocks and pebble beaches in the lake, no combined carbonic acid could be detected in the water; indeed, there would be no base for it to combine with. On the other hand, small quantities of free carbon dioxide were present dissolved in the water, and were estimated by Tornøe's method.*

	A.	B.
Free carbon dioxide in solution ..	0.028 %	0.017 %

Result A was the mean of two determinations which agreed to within 0.002 per cent, and result B was obtained twice by the use of different standard solutions; the results were identical.

No iodine or bromine could be detected in the small quantity of water available for examination.

Spectroscopic examination revealed the presence of a trace of barium. The quantity present would have been quite unweighable, and although estimated with the calcium could not have vitiated the results.

The results given under the heading B are regarded as those which most nearly represent the true condition of the lake, and consequently no attempt has been made to strike an average between the two series of results. The A results are given *in extenso*, in order to demonstrate the degree of reliability of the B results, a matter which will be of importance in the future, when, after an interval of some years, another investigation of the water of Lake Urmi is made.

City and Guilds of London Institute.—The Research Fellowships founded by the Salters' Company and the Leathersellers' Company for the encouragement of higher research in Chemistry in its relation to manufactures, tenable at the City and Guilds Central Technical College, being now vacant, the Executive Committee of the City and Guilds of London Institute will, before the commencement of next session, consider applications and elect candidates. The grant made by each of the Companies to the Institute for this purpose is £150 a year. Copies of the schemes under which the Fellowships will be awarded may be had on application to the Honorary Secretary of the Institute, Gresham College, Basinghall Street, E.C.

* Before applying Tornøe's method for the estimation of carbon dioxide to the samples of water A and B, two determinations of combined carbon dioxide in a dilute and standard solution of sodium carbonate were carried out in order to ascertain the degree of accuracy one might hope for. In the first, the carbon dioxide found only exceeded that known to be present by 0.0003 gm. and in the second by 0.0001 gm.

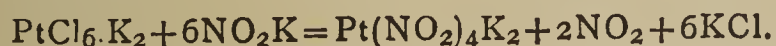
ON THE COMPLEX SALTS OF PLATINUM:
PLATO-OXALONITRITE OF POTASSIUM.

By M. VÉZES.

WE have seen in a previous paper (*Bull. Soc. Chim.*, Series 3, vol. xxi., p. 143), how the reactions which unite the plato-oxalate and the platonitrite of potassium give, as an intermediate product a mixed salt, very stable in aqueous solution, the plato-oxalonitrite of potassium, $\text{Pt}(\text{CO}_2.\text{CO}_2)(\text{NO}_2)_2\text{K}_2 + \text{H}_2\text{O}$. The study of these reactions has shown that the simplest way to obtain this plato-oxalonitrite consists in causing oxalic acid to react on platonitrite of potassium. We will now describe the method which should be followed in preparing this body, starting from metallic platinum, as well as the properties of the salt formed.

I. There are two methods of preparing platonitrite of potassium from metallic platinum (*Ann. Chim. Phys.*, Series 6, vol. xxix., p. 158); in the first, the solution of the metal in aqua regia is transformed successively into chloroplatinate of potassium, then into chloroplatinite (*Bull. Soc. Chim.*, Series 3, vol. xix., p. 879), which is then treated with nitrite of potassium; the other consists in making this latter salt act directly on the chloroplatinic solution. The second of these two methods is decidedly more rapid than the other, and does not require the use of pure platinum; for these two reasons it is preferable to the former. It is true that it is more expensive, the amount of nitrite of potassium necessary being much greater; but a part of this nitrite can be, as we shall see later on, replaced by carbonate of potassium, which will greatly diminish the difference in cost of the two processes.

The method of working is as follows:—Spongy commercial platinum is dissolved in warm aqua regia. The solution is evaporated almost to dryness, and the residue taken up with warm water. Nitrous vapours are given off, and we obtain a solution of chloroplatinic acid, still containing traces of nitrated products. To this solution, diluted to about 2 litres, and heated in a large porcelain crucible, is added about 70 grms. of pure carbonate of potassium, which is thrown in in the solid state, a little at a time, while constantly agitating, to help the attack on the salt and the escape of carbonic acid. The chloro-platinic acid is thus changed into chloroplatinate of potassium, which remains in suspension in the solution. To this mixture, which must be boiled and to which water must be added from time to time to maintain its volume, we gradually add pure solid nitrite of potassium. This salt is dissolved with a slight disengagement of nitrous fumes, and the resulting liquid gradually re-dissolves all the chloroplatinate in suspension, so as to give finally an almost clear liquid of a greenish-yellow colour with a distinctly alkaline reaction. This result is attained by using about 350 grms. of pure commercial nitrite of potassium containing about 80 per cent of actual nitrite, though a little more than is required by the equation showing the transformation of the chloroplatinate into the platonitrite—



The solution thus obtained, freed by filtration from the slight precipitate which it might contain (oxides of the commoner metals, double potassic nitrites of iridium and rhodium), is left to cool; it gives an abundant deposit of anhydrous platonitrite, which is drained and re-crystallised in boiling water. This re-crystallisation gives about 200 grms. of the hydrated platonitrite, $\text{Pt}(\text{NO}_2)_4\text{K}_2 + 2\text{H}_2\text{O}$.

The salt thus obtained is then re-dissolved in about 2 litres of warm water, and an excess (100 grms.) of crystallised oxalic acid is added. On boiling, the acid is dissolved, colouring the liquor green, and abundant nitrous fumes are given off. When this ceases and the solution becomes yellow it is allowed to cool, and the oxalonitrite crystallises out. We thus obtain by the first

operation about 160 grms. of very pure salt; the mother-liquor conveniently concentrated will still give another 50 grms.

II. The salt thus prepared is in the form of bright yellow prismatic crystals. Under the microscope these crystals have the general appearance of a parallelogram of which the acute angle is about 68° ; they act on polarised light, and have a position of extinction about 25° from one of the sides of the parallelogram.

The crystallographic examination of this salt, kindly made by M. Goguel, has given the following results:—

The crystals are monoclinic, citron-yellow, transparent, brilliant, and with very distinct facets; they are elongated along the zone $h'(100) g'(010)$, and flattened along g' . They present the facets g' dominant, $m(110)$, $p(001)$, $e\frac{1}{2}(011)$, $a'(\bar{1}01)$. Their dimensions are from 3 to 4 m.m. in length, 2 m.m. wide, and about $\frac{1}{2}$ m.m. thick.

	Angles.	Measured.	Calculated.
$\{m g'\}$	$(110) (010) \dots$	$66^\circ 2'$	
$\{m n\}$	$(110) (110) \dots$	$47^\circ 56'$	$47^\circ 56'$
$\{g' e'\}$	$(010) (011) \dots$	$70^\circ 6' 10''$	$70^\circ 14'$
$\{e' p\}$	$(011) (001) \dots$	$19^\circ 54' 55''$	$19^\circ 46'$
$\{g' p\}$	$(010) (001) \dots$	$90^\circ 1' 5''$	90°
$\{m e'\}$	$(110) (011) \dots$	$63^\circ 27' 45''$	$63^\circ 27' 25''$
$\{e' a'\}$	$(011) (\bar{1}01) \dots$	$50^\circ 51' 50''$	
$\{a' m \text{ adj}\}$	$(\bar{1}01) (\bar{1}10) \dots$	$63^\circ 41' 15''$	
$\{p a'\}$	$(001) (\bar{1}01) \dots$	$47^\circ 52' 51''$	
$\{p h'\}$	$(001) (100) \dots$	$47^\circ 52' 51''$	$68^\circ 20' 9''$

These measurements lead to the parameters:—

$$a : b : c :: 0.4131 : 1 : 0.3340,$$

$$\beta = 111^\circ 39' 51''.$$

If we examine the optical properties in the plane g' we observe that the plane of the optical axes is perpendicular to g' , making an angle of about 25° with the direction $h'g'$ in the obtuse angle ph' . These axes are very wide apart, their acute bisectrix appears to be in g' .

When dried in the cold by compression between filter papers the plato-oxalonitrite of potassium is undecomposed in the air.

Heated to 100° it effloresces and loses a molecule of water of crystallisation. This dehydration is rather slow; if we do not exceed 110° we may have to go on heating for several days before obtaining a residue of a constant weight. It is much more rapid at about 130° .

If we continue to raise the temperature of the salt thus dehydrated, a very lively reaction becomes manifest at about 240° . At this point a sort of boiling takes place, which soon permeates the whole mass, and the salt, which was of a greyish colour since it began to effloresce, rapidly changes to black. The gas given off in this transformation, and which causes this boiling up, is entirely composed of carbonic acid, and does not contain a trace of nitrous fumes. As for the black residue, it is formed of platinum and nitrite of potash. This destruction of the plato-oxalonitrite by heat should therefore be according to the formula $\text{Pt}(\text{CO}_2.\text{CO}_2)(\text{NO}_2)_2\text{K}_2 = \text{Pt} + 2\text{NO}_2\text{K} + 2\text{CO}_2$, an equation which is justified by the figures quoted further on when dealing with the analysis of this salt.

The plato-oxalonitrite, though not very soluble in cold water, becomes much more so as the temperature rises; in fact it dissolves in seven times its weight of boiling water, and in sixty times its weight of cold water. It is thus much less soluble in the cold than the plato-nitrite, which requires twenty-seven times its weight of water at 15° . Consequently it is still more easily purified by re-crystallisation than the platonitrite.

This slight solubility in cold water is susceptible of an important application. When we effect the separation of the platinum metals by the nitrite method (A. Joly and E. Leidié, *Comptes Rendes*, vol. cxix., p. 1259), the platinum is separated from the allied metals in the form

TABLE I.

		Calculated.		Found.					
				I.	II.	III.	IV.	V.	VI.
Pt	194.8	41.34	—	41.57	41.55	41.33	41.06	41.64	—
2K	78.3	16.62	—	16.50	16.57	—	16.64	16.60	—
2C	24.0	5.09	—	—	—	5.09	—	—	—
2N	28.1	5.96	—	—	—	5.95	—	—	—
8O	128.0	27.17	—	—	—	—	—	—	—
H ₂ O	18.0	3.82	3.92	3.60	3.84	—	—	—	—
Pt(CO ₂ ·CO ₂)(NO ₂) ₂ K ₂ +H ₂ O ..	471.2	100.00	—	—	—	—	—	—	—
Pt+2NO ₂ K	365.2	77.50	77.44	77.88	77.70	—	—	78.07	—
Pt+SO ₄ K ₂	369.1	78.33	—	78.30	78.43	—	78.10	78.59	—
2CO ₂	88.0	18.68	18.64	18.52	18.46	18.65	—	—	—

TABLE II.

		Calculated.		Found.				
				I.	II.	III.	IV.	V.
Pt	194.8	41.34	41.81	41.64	—	—	—	—
2K	78.3	16.62	16.25	16.49	—	—	—	—
2C	24.0	5.09	—	—	5.58	5.50	5.35	—
2N	28.1	5.96	—	—	5.75	5.58	5.73	—
8O	128.0	27.17	—	—	—	—	—	—
H ₂ O	18.0	3.82	—	—	3.89	—	—	—
Pt(CO ₂ ·CO ₂)(NO ₂) ₂ K ₂ +H ₂ O ..	471.2	100.00	—	—	—	—	—	—
Pt+2NO ₂ K	365.2	77.50	77.25	77.80	—	—	—	—
Pt+SO ₄ K ₂	369.1	78.33	77.99	78.34	—	—	—	—
2CO ₂	88.0	18.68	—	—	20.44	20.15	19.61	—

of platonitrite of potassium. The transformation of this salt into the oxalonitrite, still more soluble in the cold, enables us to obtain this metal in a much purer state; and the decomposition by heat of this oxalonitrite, followed by several washings with warm water, enables us to immediately recover the metal. If we take the precaution to pulverise the oxalonitrite very finely before submitting it to the action of heat, we should obtain pure platinum in a very fine state of division, and consequently in a very convenient form for studying the reactions of this metal.

The aqueous solution of the oxalonitrite is very stable; like that of the platonitrite, it can be boiled and evaporated to dryness without decomposing the salts it contains.

Oxalonitrite of potassium is insoluble in alcohol.

III. The methods formerly employed for the analysis of the complex nitrated salts of platinum (*Ann. Chim. Phys.*, Series 6, vol. xxix., p. 149-158), are applicable without much modification to the case of the plato-oxalonitrite and its derivatives.

The estimation of the carbon is made in the state of carbonic acid gas, of which the volume is measured at the same time as that of the nitrogen (*loc. cit.*, p. 150), with the aid of a column of cupric oxide in the combustion tube.

The estimation of the platinum and the potassium is effected by heating the salt to about 300°; this eliminates all the carbon in the state of carbonic acid gas. This operation is carried out over a Bunsen burner, the small porcelain crucible in which the analysis is carried out being covered with a small watch-glass, by which all loss from projection is avoided. Its use further enables us to control the estimation of the water of crystallisation; if the dehydration is not complete traces of water retained by the salt will show on the surface of the glass. The residue from this calcination, consisting of platinum and nitrite of potassium, is then treated with a slight excess of dilute sulphuric acid, then evaporated to dryness and calcined in an atmosphere of carbonate of ammonium. The estimation is completed as has already been described (*loc. cit.*, pp. 155 and 157, Method VI.).

Analysis of the Plato-oxalonitrite.—The formula

Pt(CO₂·CO₂)(NO₂)₂K₂+H₂O, attributed above to the material dried in the cold between filter papers, results from the following analyses. The analyses I., II., III., and IV. were performed on material obtained by the platonitrite and oxalic acid; analysis V. on a product obtained by the plato-oxalate and nitrite of potassium (*Bull. Soc. Chim.*, Series 3, vol. xxi., p. 146); analysis VI., on a product obtained by the plato-dichloronitrite, and the neutral oxalate of potassium (*loc. cit.*, p. 147).

I. 1.1926 grms. of material, heated to 110°, lost 0.0468 grm. of water; the dry product, heated to about 300°, lost 0.2223 grm. of carbonic acid, leaving a residue of 0.9235 grm.

II. 1.1143 grm. of material, heated to 110°, lost 0.0401 grm. of water; the dry product, heated to about 300°, lost 0.2064 grm. of carbonic acid, leaving a residue of 0.8678 grm., which, heated to redness with an excess of sulphuric acid, gave 0.4632 grm. of platinum and 0.4093 grm. of sulphate of potassium, containing 0.1839 grm. of potassium.

III. 0.8651 grm. of material, heated to 110°, lost 0.0329 grm. of water. The dry product, heated to about 300°, lost 0.1580 grm. of carbonic acid, leaving a residue of 0.6652 grm., which, heated to redness with an excess of sulphuric acid, gave 0.3557 grm. of platinum and 0.3157 grm. of sulphate of potassium (containing 0.1418 of potassium).

IV. 1.5381 grms. of material, heated to redness with an excess of tungstic acid, gave 73 c.c. of nitrogen at 0° and 760 m.m. (weighing 0.0916 grm.), and 146 c.c. of carbonic acid at 0° and 760 m.m. (weighing 0.2869 grm., and containing 0.0782 grm. of carbon). The contents of the boat, after dissolving the tungstic acid in an alkali, gave 0.6357 grm. of platinum.

V. 0.5631 grm. of material, heated to redness with an excess of sulphuric acid, gave 0.2312 grm. of platinum and 0.2086 grm. of sulphate of potassium (containing 0.0937 grm. of potassium).

VI. 0.3115 grm. of material, heated to 300°, left a residue of 0.2432 grm., which, heated to redness with an excess of sulphuric acid, gave 0.1297 grm. of platinum and 0.1151 grm. of sulphate of potassium (containing 0.0517 grm. of potassium). (See Table I.).

Analysis of the Greenish Salt.—Below we give the analysis of the greenish crystals, the production of which has already been described (*Bull. Soc. Chim.*, Series 3, xxi., p. 145)—analyses from which we may conclude that these green crystals are plato-oxalonitrite modified in appearance by admixture with a small quantity of plato-oxalate. In fact we have found a little more carbon and a little less nitrogen than would be contained by the normal plato-oxalonitrite. The Analyses I., II., III., and IV. were carried out on products obtained by the platonitrite and an excess of oxalic acid; the Analysis V. on a product obtained by treating the dark coloured plato-oxalate of potassium with a small quantity of nitrite of potassium (*loc. cit.*, p. 146).

I. 0.6786 grm. of material, heated to about 300°, left a residue of 0.5242 grm., which, heated to redness with an excess of sulphuric acid, furnished 0.2837 grm. of platinum and 0.2455 grm. of sulphate of potassium (containing 0.1103 grm. of potassium).

II. 0.5171 grm. of material, heated to about 300°, left a residue of 0.4023 grm., which, heated to redness with an excess of sulphuric acid, furnished 0.2153 grm. of platinum and 0.1898 grm. of sulphate of potassium (containing 0.0853 grm. of potassium).

III. 0.5711 grm. of material, heated to 120°, lost 0.0222 grm. of water. The dry residue, heated to redness with tungstic acid, gave 26.2 c.c. of nitrogen at 0° and 760 m.m. (weighing 0.0329 grm.), and 59.4 c.c. of carbonic acid at 0° and 760 m.m. (weighing 0.1167 grm. and containing 0.0318 grm. of carbon).

IV. 0.5276 grm. of material, heated to redness with tungstic acid, gave 23.5 c.c. of nitrogen at 0° and 760 m.m. (weighing 0.0294 grm.), and 54.1 c.c. of carbonic acid at 0° and 760 m.m. (weighing 0.1063 grm. and containing 0.0290 grm. of carbon).

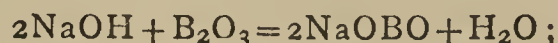
V. 0.6534 grm. of material, heated to redness with tungstic acid, gave 29.9 c.c. of nitrogen at 0° and 760 m.m. (weighing 0.0375 grm.), and 65.2 c.c. of carbonic acid at 0° and 760 m.m. (weighing 0.1281 grm., and containing 0.0349 grm. of carbon). (See Table II.).—*Bull. Soc. Chim.*, Series 3, xxi., No. 10.

A VOLUMETRIC METHOD FOR THE ESTIMATION OF BORIC ACID.*

By LOUIS CLEVELAND JONES.

WHEN boric acid and mannite are mixed in solution, a peculiar compound of strongly acid properties is the result. This compound decomposes carbonates, and its acid taste is comparable to that of citric acid, much stronger than that of boric acid alone. Magnanini (*Gaz. Chim.*, xx., 428-440; xxi., 134-145) has found that the product of such a mixture of boric acid and mannite solutions shows greater electrical conductivity and a lower freezing-point than a similar molecular solution of either substance alone. Other polyatomic alcohols (but all to a less degree than mannite) and some organic acids show this peculiar property of combining chemically with boric acid to increase its acid qualities (Klein, *J. Pharm. Chem.*, [4], vol. xxviii.; Lambert, *Compt. Rend.*, cviii., 1016, 1017). Of this reaction between boric acid and the polyatomic alcohols, Thomson (*J. S. C. I.*, xv., 432), Barthe (*J. Pharm. Chim.*, xxix., 163), and Jörgensen (*Zeitschr. f. Angew. Chem.*, 1897, 5) have taken advantage to develop methods for the volumetric estimation of boric acid. Glycerin is used to form a combination with boric acid, sufficiently acidic to give an acid reaction when used with a sensitive indicator and make possible its titration with an alkaline solution. Höning and Spitz (*Zeitschr. f. Angew. Chem.*, 1896, 549) show that in the method of

Jörgensen a very large amount of glycerin must be used to prevent the appearance of the indication of alkalinity with phenolphthalein before all the boric acid is neutralised according to the following equation:—



that in the presence of carbonates the solution must be boiled to decompose bicarbonates, and the escape of boric acid by volatilisation prevented by the use of a return condenser; and that silica must be removed by the process of Berzelius, and the solution then neutralised by the use of methyl orange before a titration of the boric acid can be made.

Vadam (*J. Pharm. Chim.* [6], viii., 109-111), for the estimation of boric acid in butter, makes use of mannite, which, as he finds, gives sharper indication with litmus than glycerin. According to this process, the solution to be analysed for boric acid is neutralised by the use of litmus and a solution of sodium hydroxide. Mannite (1-2 grms.) is then added, bringing about an acid reaction with the boric acid present in free condition. The solution is then titrated to alkalinity by sodium hydroxide.

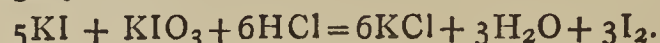
None of the above methods with glycerin have, in my experience, given anything but comparatively crude results. The weak acidic properties of boric acid, the interference (and difficulty of removal) of carbon dioxide with all organic indicators sufficiently delicate to be used with boric acid, and, indeed, the procuring of a standard alkali containing no carbonate, together with the supposed detrimental influence of silica and the lack of a convenient method for its removal, have made the process of Gooch (*Amer. Chem. Journ.*, ix., 23-33; Moissan, *Compt. Rend.*, cxvi., 1087; Kraut, *Zeitschr. f. Anal. Chem.*, xxxvi., 165; Montemartini, *Gaz. Chim. Ital.*, xxviii., 1, 344), which involves distillation and weighing with calcium oxide, the only means (though requiring long time and exceeding care) in use for the accurate separation and estimation of boric acid. Recently sodium tungstate has been recommended from this laboratory (Gooch and Jones, *Amer. Journ. of Science*, vii., 34) as a substitute for calcium oxide to retain the distilled boric acid. The entire process, however, is one of the most exacting in analytical chemistry, and for this reason a convenient, rapid—and at the same time accurate—method for the estimation of boron is especially desirable. The first step toward the development of such a process must be the convenient preparation and the accurate estimation of the standard solution of alkali to be used for neutralising the boric acid. This has been found to be easily accomplished by the process recommended by Kübler (*Zeitschr. f. Anorg. Chem.*, xiii., 124-150). This observer, in an extensive investigation of the analytical methods for the volumetric estimation of alkaline and alkali carbonates in solution, finds that both phenolphthalein and methyl orange are appreciably sensitive to carbonic acid; but when this interfering agent is removed by precipitation with barium chloride according to the process of Winkler (Massanalyse), the remaining free alkali may be estimated with great accuracy by phenolphthalein and decinormal hydrochloric acid.

Obviously, if the difficulties dependent upon the action of carbon dioxide can be obviated, and if the acidity of the boric acid can be increased to such an extent that a sufficiently sensitive indicator will give with accuracy the neutralisation-point with free alkali, and if the alkali and stronger acid can be combined while boric acid alone remains free, then it should be possible to estimate boric acid volumetrically. Experiment has shown that barium chloride removes carbon dioxide, and that mannite makes a combination with boric acid strongly acidic to phenolphthalein.

To obtain the boric acid alone in free condition many attempts have been made. Gladding (*Journ. Am. Chem. Soc.*, iv., 568), Thaddeff (*Zeitschr. f. Anal. Chem.*, xxxvi., [9], 568), and Rosenblatt (*Zeitschr. f. Anal. Chem.*, xxvi., 18) have isolated the boric acid by distillation with methyl

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, Fourth Series, vol. vii., February, 1899.

alcohol and a non-volatile acid. Many indicators theoretically insensible to free boric acid have been used to indicate the neutralisation of the stronger acids. Hönig and Spitz (*Zeitschr. f. Anorg. Chem.* [18], 549) and Thomson (*J. S. C. I.*, xv., 432) use methyl orange, Morse and Burton (*Am. Chem. Journ.*, x., 154) tropæolin oo, while Vadam (*J. Pharm. Chim.*, [6], viii., 109-111) makes use of litmus. All these indicators, however, have been found by experiment to be more or less affected by boric acid in solution. On the other hand, I have found in the well-known reaction, according to which a stronger acid liberates regularly iodine from a mixture of iodide and iodate, the solution of this difficulty. If both the iodide and iodate are in excess of the acid the entire amount of free acid will be neutralised, and the corresponding amount of iodine liberated according to the following equation:—



This liberated iodine may be removed by sodium thiosulphate, and a solution obtained which is absolutely neutral, containing only neutral salts, potassium iodide, iodate, and tetrathionate. The statements made by P. Georgevic (*J. Prac. Chem.*, xxxviii., 118) and Furry (*Am. Chem. Journ.*, vi., 341), that boric acid present in moderate amount in solution has not the slightest action on a mixture of iodide and iodate, have been experimentally verified. Therefore when this acid is liberated by an excess of a stronger acid, and the iodine set free destroyed by thiosulphate, it remains free in solution to be titrated in any convenient matter possible.

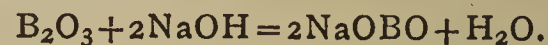
Following along the lines suggested by the above reactions, a volumetric process for the estimation of boric acid has been developed. For a basis of the investigations, a standard solution of boric acid was prepared by dissolving in a litre of water about 8 grms. of carefully weighed anhydrous boric oxide. This anhydrous boric oxide was prepared from the several times re-crystallised hydrous boric acid by long-continued fusion over a blast-lamp. A solution of approximately $n/5$ sodium hydroxide was prepared from the ordinary sodium hydroxide of the laboratory. The free alkali in this solution was estimated by the process of Winkler recommended by Kübler. The acid used to make this estimation was hydrochloric, standardised by silver nitrate.

The full method for the estimation of boric acid as finally elaborated is as follows:—The solution is made clearly acid to litmus by hydrochloric and 5 c.m.³ of a solution (10 per cent) of barium chloride added. An amount of iodate and iodide of potassium sufficient to liberate an amount of iodine at least equivalent to the excess of hydrochloric acid in the acidified solution is mixed with starch in a separate beaker, and the iodine, which is usually thrown out by this mixture, is just bleached by a dilute solution of thiosulphate.

To the now neutral solution of iodide and iodate a single drop of the solution to be analysed is transferred by a glass rod. If a blue colouration is developed, the solution is acidic with hydrochloric acid, and all the boric acid is in free condition. The amount of iodide and iodate used depends upon the acidity of the solution containing boric acid. Usually 10 c.m.³ of a 25 per cent solution of iodide and the same amount of a saturated solution of iodate is sufficient. Any larger excess of hydrochloric acid should be neutralised by sodium hydroxide before the iodide and iodate mixture is added. After the addition of the iodide and iodate solution, containing starch, to the boric acid solution, the liberated iodine should be carefully bleached by thiosulphate. Any excess of thiosulphate in reasonable amount does not seem to be detrimental, but in practice the starch iodide colour is clearly bleached, and no more then added. Carbonates prevent a definite indication of the neutral point by thiosulphate and starch iodide, therefore the barium chloride (about 5 c.m.³) should be added before this point in the process. The mixture of iodide and iodate is not

added to the solution to be analysed until after it is made acidic, for the reason that when the neutral point is approached by the addition of hydrochloric acid, the starch iodide is thrown out locally by the acid, and the small amount of sodium borate remaining undecomposed does not again bleach the colouration produced, thus obscuring the neutral point which must be obtained before titrating for boric acid.

The solution after the bleaching of the iodine by thiosulphate is colourless, and contains only starch, neutral chloride, potassium tetrathionate, iodide and iodate, and all the boric acid present in uncombined condition. The carbonate lies out of the sphere of action in insoluble form as barium carbonate. A few drops of the indicator, phenolphthalein, are now added, and the alkaline solution run in until a strong red colouration is produced. A pinch of mannite is then added, which bleaches the phenolphthalein colouration, and the alkali solution again run in to a faint indication, which, if permanent on the addition of more mannite, may be taken as the reading-point. About 1—2 grms. of mannite are necessary for a determination. The boro-mannite compound is sufficiently acidic to liberate iodine abundantly, but it appears to be a time reaction, and at the end of six hours only about 95 per cent of the theoretical amount (considering B_2O_3 as a bivalent acid) has been thrown out. The combination of boric acid and mannite liberates in the presence of iodide and iodate immediately only about one-half the iodine required on the theory that B_2O_3 under these conditions acts as a bivalent acid, or with the neutralising power of metaboric acid, HOBO . When no mannite is present phenolphthalein gives an alkaline indication when only about one-half the amount of alkali theoretically necessary to form the metaborate, NaOBO , has been added. Obviously, then, the starch iodide colouration will not appear at all on the addition of mannite, if about one-half the free boric acid is first neutralised by the solution of alkali, and the remainder of the alkali immediately added to complete neutralisation. The point at which the danger of the appearance of the iodide colouration on the addition of mannite has been passed, is roughly indicated before the mannite has been added by the appearance of the strong alkaline indication of phenolphthalein. This indicator would not need to be added at all, if the boro mannite compound quickly and regularly liberated iodine from the iodide and iodate. The fact, however, that this compound of boric acid and mannite—as has been ascertained by experiment, liberates, on standing twelve hours, about 99 per cent of the theoretical amount of iodine, places the strength of this acid above that of citric or tartaric acid as investigated by Furry (*Am. Chem. Journ.*, vi., 341). With phenolphthalein, however, the end reaction is sharp, and the small amount of carbonate present in the standard solution of alkali is precipitated by the barium chloride already in the solution. The calculation must therefore be based on the amount of free hydroxide in the standard solution of alkali used, according to the following representation:—



The best results and the most definite indications are obtained in cold solution of a volume not greater than 50 c.m.³. This fact accords with the observations of Magnanini (*Gaz. Chim.*, xx., 428, and xxi., 134), that the relative electrical conductivity of the boro-mannite solution is decreased by dilution and elevation of the temperature. When silicates are present in solution the silicon dioxide is liberated by the excess of hydrochloric acid, and this oxide, whether in hydrous or anhydrous condition, neither affects the indication with iodine nor phenolphthalein, nor does it form with mannite a compound of acidic properties. Ammonium salts interfere with the indication given by phenolphthalein, and may be removed by boiling with potassium hydroxide in excess, or an indicator used not affected by them.

To test the action of fluorides in the process, several experiments were made in which hydrofluoric acid (10 c.m.³ of *n*/10 solution) was introduced into the solution containing salts of sodium, free hydrochloric and boric acids. Barium chloride was then added, and the analysis for boric acid completed in the usual way without the accuracy of the results being in any way interfered with by the presence of hydrofluoric acid.

The following table contains the results of a series of analyses in which the boric acid was first drawn into an excess of sodium hydroxide, then estimated according to the method described.

The standard solutions of boric acid used contained—I., 7.153 grms., and II., 7.706 grms. per litre. The solution of free sodium hydroxide was 0.21427 normal.

TABLE I.

	B ₂ O ₃ Sol. taken. C.m.s.	NaOH Sol. required C.m.s.	B ₂ O ₃ taken. Grm.	B ₂ O ₃ found. Grm.	Errors on B ₂ O ₃ . Grm.
I.	1. 21.95	21.02	0.1571	0.1577	+0.0006
	2. 20.68	19.65	0.1479	0.1474	-0.0005
	3. 20.73	19.63	0.1483	0.1473	-0.0010
	4. 23.05	23.71	0.1776	0.1777	+0.0001
	5. 23.10	23.80	0.1780	0.1783	+0.0003
II.	6. 22.76	23.35	0.1754	0.1750	-0.0004
	7. 24.08	24.78	0.1855	0.1857	+0.0002
	8. 22.00	22.50	0.1695	0.1686	-0.0009
	9. 20.78	21.28	0.1601	0.1595	-0.0006

Practical tests of the method were made upon specimens of crude calcium borate and colemanite.*

The finely-ground minerals were dissolved in hydrochloric acid, and the analyses proceeded with as above described.

Analysis of Crude Borate of Lime.

TABLE II.

	Ca borate taken. Grm.	B ₂ O ₃ found. Grm.	B ₂ O ₃ in per cent.
1.	0.4016	0.2289	56.99
2.	0.4044	0.2302	56.92
3.	0.4000	0.2285	57.11

Analysis of Colemanite.

TABLE III.

	Mineral taken. Grm.	B ₂ O ₃ found. Grm.	B ₂ O ₃ p.c.	
1.	0.4034	0.2064	51.15	
2.	0.4070	0.2069	50.80	
3.	0.6004	0.3054	50.86	
4.	0.6006	0.3056	50.89	
5.	0.5059	0.2592	51.24	
6.	0.5092	0.2592	50.89	
				Average. 50.99 %

An analysis for boric acid by this process can be completed in five minutes, and the results are obviously accurate within the limits of ordinary analysis.

The usually interfering substances, fluorine, silica, and carbon dioxide, have no detrimental influence on the results of this process.

A NEW VOLUMETRIC METHOD FOR THE DETERMINATION OF COPPER.†

By RICHARD K. MEADE.

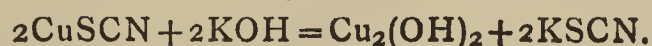
THE average analyst is often deterred from the use of a volumetric method by the necessity of making and standardising a special solution. In many cases it takes nearly as much time to ascertain the strength of the required solution as it does to make the analysis itself,

and the standardisation and analysis together render the volumetric method frequently as slow, if not slower, and vastly more troublesome than the gravimetric determination.

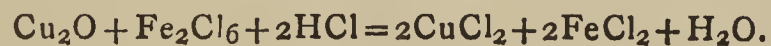
Volumetric analysis, therefore, becomes more and more an ideal method of quantitative determination as it approaches the requirement of a single standard solution, capable of having its strength accurately determined by simple means, giving a single, definite, clear-end reaction.

In iron and steel laboratories permanganate is fast coming to the front as a help to rapid analysis. Iron, phosphorus, manganese, sulphur (Payne's iodine solution is prepared by adding standard permanganate to potassium iodide), and calcium can all be quickly determined by the use of one standard solution. While it may never be possible to supplant other standard solutions by permanganate, still the sphere of its usefulness is a large one and is constantly enlarging.

For a year or more I have been experimenting upon a new method for the determination of copper by permanganate, which seems to possess many points of superiority over the old one of reduction by grape-sugar. In general it is as follows:—The copper is brought into solution as a sulphate, either by dissolving it in sulphuric acid or evaporation of its solution with sulphuric acid. The greater part of the free acid is neutralised by ammonia, the solution warmed, sulphurous acid added until the solution smells strongly of the reagent, and then a slight excess of ammonium or potassium thiocyanate (Rivot, *Compt. Rend.*, xxxviii., 868; and Busse, *Zeitschr. Anal. Chem.*, 1878, 55). The copper is immediately precipitated as cuprous thiocyanate. Stirring and warming renders the precipitate heavy and easily handled. The solution is filtered through asbestos, using the pump, and well-washed. The precipitate and filter are thrown into the beaker in which the precipitation was made and heated with a solution of caustic soda or caustic potash. Double substitution takes place. Hydrated cuprous oxide and potassium or sodium thiocyanate result:—



The oxide is filtered on asbestos and washed well with hot water. The precipitate and filter are again placed in the same beaker and an excess of ferric chloride or ferric sulphate (free from nitric acid, free chlorine, or ferrous salts), together with a little dilute sulphuric acid, added. The copper oxide reduces a corresponding amount of iron from the ferric to the ferrous condition:—



The beaker is warmed and stirred until all the copper oxide is dissolved. The solution is then poured through a perforated platinum disk, and the asbestos which stays behind upon it washed with water, to which has been added a little sulphuric acid and a little ferric chloride or sulphate. The solution is then titrated with permanganate. The iron equivalent to the permanganate used multiplied by 1.125 gives the weight of copper in the sample.

Instead of sulphurous acid, ammonium or sodium bisulphite may be used to reduce the copper. A solution of equal weights of sodium bisulphite and potassium thiocyanate answers well as a reagent for the precipitation of the metal. Since copper is the only metal precipitated by an alkaline thiocyanate from an acid solution, the presence of arsenic, antimony, bismuth, zinc, and other materials which render the electrolytic, the cyanide, and the iodine method inaccurate, will not affect the results.

The caustic alkali solution, used to convert the cuprous thiocyanate into cuprous hydroxide, must not be too strong, or some of the metal will go into solution, colouring the liquid blue. I have used about a half normal solution of caustic potash, made by dissolving 28 grms. of the salt in a litre of water. Either ferric sulphate or ferric chloride may be used to dissolve the cuprous oxide. The former is probably the safest, but

* These specimens were kindly furnished by Dr. C. A. Crampton, of Washington, whom I desire to thank for this courtesy.

† Contribution from the Chemical Laboratory of Lafayette College. From the *Journal of the American Chemical Society*, vol. xx., No. 8,

the latter appears to dissolve the precipitate the more readily of the two.

As a test of the accuracy of the method 4 grms. of pure electrolytic copper were dissolved in nitric acid and the solution evaporated with sulphuric acid until the nitric acid was expelled. The solution was cooled and diluted to 1 litre. The copper contained in 50 c.c. was then determined electrolytically with the following result:—

	Grm.
1.	0.2003
2.	0.2003
3.	0.2000
4.	0.1997
Average	0.2001

The copper in 50 c.c. was next determined by the thiocyanate-permanganate method outlined above. The permanganate solution used was made by dissolving 5.02 grms. of pure crystallised potassium permanganate in water, and diluting, after standing twenty-four hours, to 2 litres. Its strength was determined by titration against iron wire and against ferrous ammonium sulphate.

Against ferrous ammonium sulphate:—

	Grm. iron.
1. One c.c. =	0.004455
2. One c.c. =	0.004456

Against iron wire:—

	Grm. iron.
3. One c.c. =	0.004460
4. One c.c. =	0.004449

Average one c.c. = 0.004455

One c.c. = $0.004455 \times 1.125 = 0.005012$ gm. copper.

Below are the results on 50 c.c. of the copper solution containing 0.2001 gm. copper by the thiocyanate permanganate method:—

No.	Permanganate. C.c.	Copper. Grm.
1.	39.6	0.1985
2.	39.5	0.1980
3.	39.6	0.1985
4.	39.7	0.1990
5.	40.0	0.2004
6.	39.8	0.1995

In determinations numbers 1, 5, and 6, ferric chloride was used to dissolve the cuprous oxide; in numbers 2, 3, and 4, ferric sulphate was used.

As a further and more practical test of the method, the copper in some samples of copper ore was carefully determined by the electrolytic, and then by the thiocyanate-permanganate method. Below are the comparative results:—

Sample.	Weight of sample. Grm.	Permanganate. C.c.	Copper by thiocyanate- permanganate method. Per cent.	Copper by electro- lytic method. Per cent.
1. Chalcopyrite I.	1.0	39.6	19.85	19.95
2. " "	1.0	39.3	19.70	19.86
3. Chalcopyrite II.	2.0	24.6	6.16	6.37
4. " "	2.0	24.8	6.21	6.30
5. Malachite ..	1.0	72.2	36.19	36.10
6. " "	1.0	72.2	36.19	36.15
7. Tetrahedrite ..	1.0	42.0	21.05	21.06
8. " "	1.0	41.7	20.90	21.18

It will be seen by the above results that the method is accurate enough for ordinary commercial purposes. In spite of its three filtrations the method is quite rapid. Not counting the time required for the solution of the ore duplicate analyses can be easily made in from a half to three-quarters of an hour.

In the writer's opinion the process is superior to both the iodine and the cyanide method. It requires the use

of no rapidly changing solutions, but one which every analyst has on hand nearly all the time. The end reaction is clear, distinct, and familiar to all chemists. The method is applicable to any ore, matte, or alloys. It is as rapid as the cyanide, except in certain cases favourable to the latter, and more rapid than the iodine method. Finally, not the least of its points of advantage is that it is more accurate than either of the two.

ON A TEST,
BY THE FREEZING-POINT METHOD,
OF THE
IONISATION COEFFICIENTS DETERMINED BY
THE CONDUCTIVITY METHOD,
FOR
SOLUTIONS CONTAINING POTASSIUM AND
SODIUM SULPHATES.*

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(Continued from p. 59).

Observed and Calculated Values of the Depression of the
Freezing-point for Simple Solutions.

THE following table contains the observations of the depression of the freezing-point of simple solutions, together with observations on solutions of about the same concentration by Loomis (*Phys. Review*, 1896, iii., 277) and Jones (*Zeit. Phys. Chem.*, 1893, xi., 536) for comparison. The depressions are expressed in centigrade degrees.

TABLE III.

Concentration gr.-eq. / litre.	Depression of Freezing-point.		Observer.
	K ₂ SO ₄ .	Na ₂ SO ₄ .	
0.03949	0.0975	—	Jones.
0.04	0.0952	0.0974	Loomis.
0.050	0.1185	0.1191	Author.
0.055	0.1296	0.1304	"
0.0579	0.1397	—	Jones.
0.060	0.1407	0.1416	Author.
0.070	0.1629	0.1638	"
0.07556	0.1792	—	Jones.
0.080	0.1851	0.1856	Author.
0.10	0.2307	—	Jones.
0.10	0.2271	0.2297	Loomis.
0.100	0.2285	0.2286	Author.
0.116	0.2655	—	Jones.
0.19685	0.42525	—	"
0.20	0.4317	0.4340	Loomis.
0.200	0.4322	0.4330	Author.
0.250	0.5295	0.5300	"
0.300	0.6240	0.6252	"
0.350	0.7196	0.7157	"
0.40	0.8134	0.8141	Loomis.
0.400	0.8128	0.8100	Author.
0.450	0.9063	0.8968	"
0.500	0.9950	0.9875	"
0.60	1.1672	1.1604	Loomis.
0.600	1.170	1.155	Author.
0.700	1.341	1.323	"

It will be seen, especially if the above results be plotted, that all three sets of observations agree very well with one another, but that mine agree better with Loomis's than with those of Jones. Their agreement with Loomis's is very close.

The following table contains the observed and calculated values of the freezing-point depressions for simple solutions, with the differences expressed as percentages of the observed values. In the calculations van't Hoff's

* From the *Transactions of the Nova Scotian Institute of Science*, vol. x., Session 1898-99.

constant was taken to be 1.86, and the expression used for the depression was—

$$\Delta = 1.86 (1 + 2a) N/2,$$

where N is the concentration of the solution in gr. equivalents per litre.

TABLE IV.—Depression of Freezing-point.

Con- centration (gr.-eq.)/l.	Potassium sulphate solutions.			Sodium sulphate solutions.		
	Ob- served.	Cal- culated.	Diff. per cent.	Ob- served.	Cal- culated.	Diff. per cent.
0.050	0.1185	0.1168	-1.4	0.1191	0.1164	-2.3
0.055	0.1296	0.1277	-1.5	0.1304	0.1272	-2.5
0.060	0.1407	0.1387	-1.4	0.1416	0.1379	-2.6
0.070	0.1629	0.1614	-1.5	0.1638	0.1591	-2.9
0.080	0.1851	0.1818	-1.8	0.1856	0.1803	-2.9
0.100	0.2285	0.2241	-1.9	0.2286	0.2221	-2.9
0.200	0.4322	0.4259	-1.5	0.4330	0.4181	-3.4
0.250	0.5295	0.5250	-0.8	0.5300	0.5115	-3.5
0.300	0.6240	0.6227	-0.2	0.6252	0.6015	-3.8
0.350	0.7196	0.7200	+0.1	0.7157	0.6907	-3.5
0.400	0.8128	0.8169	+0.5	0.8100	0.7782	-3.9
0.450	0.9063	0.9131	+0.8	0.8968	0.8663	-3.4
0.500	0.9950	1.0118	+1.7	0.9875	0.9532	-3.5
0.600	1.170	1.209	+3.3	1.155	1.128	-2.3
0.700	1.341	1.406	+4.9	1.323	1.303	-1.5

The above table shows the degree of accuracy with which the depression of the freezing-point can be calculated in the case of simple solutions. If the ionisation coefficients for the mixtures are determined by Prof. MacGregor's method as closely as they are for the simple solutions by putting $a = \mu/\mu_{\infty}$, the differences between the calculated and the observed values of the depressions in the case of the mixtures may be expected to be no greater than those of the above table.

(To be continued).

THE PHYSIOLOGICAL EFFECT OF CREATIN AND CREATININ, AND THEIR VALUE AS NUTRIENTS.*

By J. W. MALLET, M.D., LL.D.,
Professor of Chemistry in the University of Virginia.

(Continued from p. 56).

Experiments upon the Physiological Effects of Creatin and Creatinin.

WITH a view to the experiments afterwards to be made on the ingestion of creatin and creatinin, it was important to know what allowance should be made for the normal daily excretion of creatinin, and, moreover, as any increase in the elimination of urea in consequence of the ingestion of the flesh bases was one of the points to be examined, it was equally important to ascertain the normal daily excretion of urea. The figures of the first of the above tables (see ante) afford a basis for the establishment of average values for the normal excretion of these two substances, and show about what range of variation from the average may be looked for. In order to make this range as small as possible, and consequently to give as much value as possible to the assumption of the average for purposes of comparison, care was taken during the whole of the time in which the physiological experiments were being carried on that the conditions of food, exercise, surrounding temperature, and sleep should be as uniform as was compatible with no very inconvenient disturbance of the ordinary habits of life. Especial attention was given to the selection of a simple mixed diet of animal and vegetable materials, not at all excessive, but fully sufficient in amount, such as could be easily had

with little change from day to day, for several weeks in succession. Without actually weighing the food consumed, a pretty close approach was made to uniformity in the quantity of each article, while the distribution in time of the meals was almost absolutely regular. The greatest variation probably was in the consumption of water in all forms, but this was of little importance, as all the samples of urine were weighed, not measured, and in all the experiments aliquot parts of the total daily excretion were employed. Judging by the values shown in the table (see p. 56), the daily excretion of urea appears to have been 28.922 grms. and that of creatinin 0.817 gm. (as direct results of determination by the process used).

Having in mind the general belief in the well-marked effects of Liebig's and other meat extracts upon the nervous system, it seemed needful, when the physiological experiments were undertaken, to proceed with some caution in the administration of pure creatin and creatinin, and to begin with prudently small doses and gradually increase them. It was found, however, by a number of preliminary experiments, that 1 or 2 grms. could be taken with no appreciable physiological effect; that 5 grms. gave rise to noticeable symptoms; and that 10 or even 15 grms. did not produce any very strongly marked or alarming impression. Not more than 15 grms. was used in any of the experiments, since it was desirable that the quantity given should not be in excess of that which, even in the case of the less soluble creatin, could be held in solution by the water of a probable minimum amount of urine excreted in twenty-four hours.

A quarter of an hour before the time for beginning an experiment the bladder was emptied, and just before the experiment determinations were made of the pulse rate, of the rate of breathing, of the bodily temperature (taken under the tongue), and of the reaction of the urine, test-paper being used. At a definite time, generally either 10 or 10.30 a.m., about two hours after breakfast, the dose of creatin or creatinin, previously reduced to fine powder, was swallowed with a little water.

With the larger doses there was perceived in a very short time—ten or fifteen minutes—a slight frontal headache, with a sense of constriction across the forehead, and slight ringing in the ears like that produced by quinine. These symptoms, which were of but trifling intensity, were accompanied by slight general nervous agitation, and did not last for more than an hour or two. For several hours there was a decided tendency to urinate frequently.

These general effects seemed to be the same for both the flesh bases, but were rather more marked in the case of creatin than in that of creatinin. No disturbance of digestion was perceptible from any of the doses used.

The pulse and respiration rates, the bodily temperature, and the reaction of the urine to litmus paper were observed at definite intervals. Exactly twenty-four hours after the time at which a dose had been swallowed, the bladder was again emptied; the whole of the urine for the intervening day, collected in a single vessel, was measured, weighed, and the specific gravity noted after the liquid had cooled to 15° C. The portions submitted to analysis were weighed.

The following table shows the amount of creatinin or creatin taken, the amount of urine excreted, and its specific gravity in seven experiments:—

Creatinin and Creatin taken and Urine Excreted.

Number of experiment.	Creatinin taken. Grms.	Urine excreted		Specific gravity of urine.
		Creatin in twenty-four taken. hours. Grms.	C.c.	
1.	5	—	1267	1.024
2.	10	—	1415	1.026
3.	15	—	1544	1.029
4.	—	3	1502	1.023
5.	—	5	1358	1.024
6.	—	10	1529	1.027
7.	—	15	1464	1.029

* Bulletin, No. 66, United States Department of Agriculture, Office of Experiment Stations.

Physiological Effect of Creatinin and Creatin.

	Pulse rate per minute.	Tempera- ture. °F.	Respiration per minute.	Reaction of urine.
<i>Experiment No. 1.—</i>				
Just before taking creatinin	81	98.5	18	Normally acid. (a)
One-half hour after taking creatinin ..	73	98.5	18	Do.
One hour after taking creatinin	69	98.6	17	Do.
Two hours after taking creatinin	70	98.5	18	Do.
Five hours after taking creatinin	79	98.6	19	Do.
<i>Experiment No. 2.—</i>				
Just before taking creatinin	80	98.3	17	Decidedly acid.
One-half hour after taking creatinin ..	70	98.2	17	A shade less acid.
One hour after taking creatinin (b)	62	97.9	15	Very faintly acid.
Two hours after taking creatinin (c)	74	98.4	18	Distinctly acid, but not quite so much so as at beginning.
Five hours after taking creatinin	83	98.3	17	Acidity fully normal.
<i>Experiment No. 3.—</i>				
Just before taking creatinin	76	98.6	19	Normally acid.
One-half hour after taking creatinin ..	66	98.3	17	Acidity a shade less than normal.
One hour after taking creatinin (d)	57	97.7	16	Perceptibly acid, but less so than at beginning.
Two hours after taking creatinin (e)	72	98.2	18	Acidity a shade less than normal.
Five hours after taking creatinin	80	98.4	17	Acidity fully normal.
<i>Experiment No. 4.—</i>				
Just before taking creatin	77	98.6	16	Normally acid.
One-half hour after taking creatin ..	76	98.5	16	Do.
One hour after taking creatin	74	98.6	17	Do.
Two hours after taking creatin	77	98.6	18	Do.
Five hours after taking creatin	79	98.5	17	Do.
<i>Experiment No. 5.—</i>				
Just before taking creatin	83	98.5	19	Do.
One-half hour after taking creatin ..	78	98.5	18	Do.
One hour after taking creatin	74	98.3	19	Distinctly less acid than at first.
Two hours after taking creatin	77	98.5	18	Nearly of normal acidity.
Five hours after taking creatin	82	98.4	18	Normally acid.
<i>Experiment No. 6.—</i>				
Just before taking creatin	79	98.5	17	Rather more than normally acid.
One-half hour after taking creatin ..	73	98.4	17	Faintly acid.
One hour after taking creatin	69	98.5	16	Slightly alkaline.
Two hours after taking creatin	69	98.1	18	Very slightly alkaline.
Five hours after taking creatin	81	98.5	16	Acidity about normal.
<i>Experiment No. 7.—</i>				
Just before taking creatin	78	98.4	17	Acidity fully normal.
One-half hour after taking creatin ..	70	98.4	18	Acidity a little less than normal.
One hour after taking creatin	67	98.3	18	Distinctly, but not strongly alkaline.
Two hours after taking creatin	65	98.2	16	Very faintly alkaline.
Five hours after taking creatin	85	98.3	18	Practically neutral; slightly inclining to acid.

(a) The exact degree of acidity was not measured by means of a standard alkaline solution, but estimated by the rapidity of development and the intensity of colour produced on litmus paper of uniform character.

(b) With frequent and well-marked intermittence.
 (c) With occasional slight intermittence.
 (d) With marked intermittence.
 (e) Intermittence scarcely perceptible.

The pulse rate, rate of respiration, body temperature, and reaction of the urine in the different tests are given in the accompanying table.

As will be seen, the most decided physiological effect produced was the retardation of the action of the heart. This was unmistakable. It seemed to be accompanied by little, if any, change in the force of impulse as felt in the radial artery; if there was any effect of this kind, it probably was a diminution of force, but there was no clear impression of such a change. The statements of others as to the flesh bases acting most perceptibly as nerve *stimulants* may perhaps be partly accounted for by smaller doses having been used by the author, and partly by evidence having been drawn from the use of meat extracts and the action of other constituents of these extracts having been confounded with the action of the pure flesh bases. The effect of creatinin as a cardiac retarder seems to be greater than that of creatin for the same dose. The latter seems also to act more slowly, this fact suggesting that its effect may be exerted, either wholly or chiefly,

after it has undergone conversion into creatinin in the body, though this is hardly probable.

In the figures obtained there may possibly be traced a slight tendency to retardation of breathing and to lowering of bodily temperature, but there is no clear evidence of this.

An interesting point is the reduction of the acidity of the urine by creatin, extending—even in the case of the larger doses—to development of an alkaline reaction. Something of the same sort is observable for the larger doses of creatinin, though not to the same extent. On noticing the results of the tests made at different times after the ingestion of the flesh bases, it will be seen that the effect upon acidity, as well as that upon the heart's action, seems to have been most marked about an hour after the doses had been taken, with some tendency to longer delay in the case of creatin than in that of creatinin. In all the experiments the reaction of the mixed total excretion for twenty-four hours was acid, and apparently of about the normal intensity.

Applying to the seven specimens of urine of these experiments the method of analysis which has been described, the following results were obtained:—

Constituents of Urine excreted in Twenty-four Hours when Flesh Bases were taken.

Number of experiment.	Urea. Grms.	Creatinin. Grms.	Creatin. Grms.
1	29.096	5.386	—
2	29.457	10.097	—
3	29.558	14.816	—
4	28.973	3.170	—
5	28.735	4.742	0.014
6	30.011	8.741	0.069
7	29.714	12.699	0.177

Examining these results, there seems to be a small increase of urea—an average of 29.363 grms. per day, as against the average of 28.922 grms. obtained from the nine samples of normal urine—and perhaps a little tendency to higher figures in the experiments in which the larger doses of the flesh bases were taken. But neither of these conclusions can be drawn with any certainty, since differences between the individual results, both in the case of normal urine and also when flesh bases were taken, were greater than the difference between the two averages.

The figures for creatinin include, of course, the amount of this substance normally present in the urine, and therefore the amount found in each experiment must be reduced by 0.817 grm., the average value for normal creatinin as found in the nine experiments first recorded. Assuming also, on the basis of the same nine experiments, that the analytical process employed yields 95 per cent of the quantity of creatinin really present, the following are the corrected results for Experiments 1, 2, and 3, when creatinin was taken:—

Corrected Results of Tests in which Creatinin was taken.

Number of experiment.	Creatinin ingested. Grms.	Creatinin recovered. Grms.	Creatinin recovered as percentage of creatinin ingested. Per cent.
1	5	4.809	96.18
2	10	9.768	97.68
3	15	14.736	98.24

As regards creatin, it is evident at a glance that nearly all of that swallowed was converted into creatinin and eliminated in this latter form, very small amounts, however, escaping and undergoing elimination unchanged. This fact of any creatin escaping change in the rapid passage through the system of a large dose is in itself an interesting point, and such an apparent result is not probably to be explained by the supposition of change in the opposite direction having occurred during the process of analysis. It is to be noticed that the quantities of creatin found as such—in all cases small—increase with increase of the dose swallowed. In order to see how far creatin was recovered, the quantity of creatinin found has first to be reduced by the allowance for that normally present, then increased in the ratio of 95 : 100, so as to correspond with the determined degree of accuracy of the analytical method used, and then calculated to the equivalent quantity of creatin which it represents—the quantity of creatin found as such must be increased in the ratio of 86.9 : 100, so as to correspond with the determined degree of accuracy of the analytical method—and finally the creatin thus found really present as such must be added to that represented by creatinin. The corrected results for experiments 4, 5, 6, and 7 are as follows:—

Corrected Results of Tests in which Creatin was taken.

Number of experiment.	Creatin ingested. Grms.	Creatin recovered as such or represented by creatinin. Grms.	Creatin recovered as percentage of creatin ingested. Per cent.
4	3	2.872	95.73
5	5	4.806	96.12
6	10	9.749	97.49
7	15	14.703	98.02

Looking at the actual quantities of creatinin and creatin recovered, it is seen that the loss on the quantity ingested does not vary largely in the several experiments, being only somewhat greater for the larger doses than the smaller; hence the relative percentage loss is less for the former than for the latter. For both urea and creatinin it has only been possible to allow for the quantity present in the urine in its natural condition on the basis of the average of the determinations made; it must be remembered that this, therefore, conceals such differences as might have appeared if the exact normal condition of the excretion could have been ascertained on the particular day on which creatin or creatinin was administered. It is, moreover, conceivable that the normal excretion of urea or creatinin, or both, may have been altered by the very ingestion of either of the flesh bases, though this is hardly likely.

(To be continued).

NOTICES OF BOOKS.

Twenty-third Annual Report of Her Majesty's Inspectors of Explosives; being their Annual Report for the Year 1898. London: Darling and Sons, Ltd. 1899.

THE Inspectors record with the deepest regret the death of their late senior colleague, Sir Vivian Dering Majendie, K.C.B. Sir Vivian had been Chief Inspector since the passing of the Act, and had been previously since 1871 in a similar position under the Gunpowder Act. It was he who was chiefly responsible for the provisions of the Explosives Act, which has now stood the test of twenty-three years working, and although many new explosives have been brought under its cognisance, and the trade has expanded in quite an unforeseen manner, the Act has proved itself equally adapted to the requirements of the present day. The vacancy in the department has been filled by the appointment of Captain Maurice Bricklade Lloyd, R.A., to be one of Her Majesty's Inspectors of Explosives.

During the past year two further modifications have taken place, the Order of the Secretary of State, No 3, having been amended in so far as it relates to the packing of small arm nitro-compounds, wet gun-cotton, and pinfire pistol cartridges, by a new Order, No. 3 (d). A copy of this order will be found in Appendix F (2).

The number of factories continues to increase, seven new ones having been added since 1897, while thirteen new licences are still under consideration. Two factories have become extinct during the year. We are glad to see that the number of deaths from accidents in manufacture has dropped from nine last year to two this year, both of these being caused by the same accident. The average annual number of deaths by accident during the decade is 4.8.

There have been added to the list of authorised explosives fourteen new substances which have successfully passed the necessary tests.

During the past year 184 visits have been made to factories, which now number 143; there has been no falling off in the general improvement referred to in previous reports, a very high standard of excellence has been reached, and we are glad to see it is fully maintained.

Proceedings for irregularities are now happily of rare occurrence; it is perhaps unavoidable that breaches of a minor character should be occasionally found, but as a rule they are at once rectified when attention is drawn to them. In two cases only was the institution of proceedings actually necessary.

The total number of magazines is now 387, being a decrease of three on last year, when the number stood at 390. There has been no case of proceedings being taken in respect of irregularities in a magazine, nor has there been any accident in one through fire or explosion during the year.

There has been a considerable decrease in the amount of foreign nitroglycerin compounds imported in 1898, as compared with 1897, the figures being respectively 983,600 lbs. and 1,153,550 lbs. The demand for foreign carbonite, which was so great in 1896, is now rapidly falling off, but the importation of foreign fireworks, principally from China and Japan, has increased from 234 tons to 325 tons. It is a matter for surprise that there can be a demand for such a large number of these articles.

The inspectors have no reason to modify the opinion already expressed by them, that the powers conferred upon them by Sections 55, 73, 74, and 75 are ample and satisfactory.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

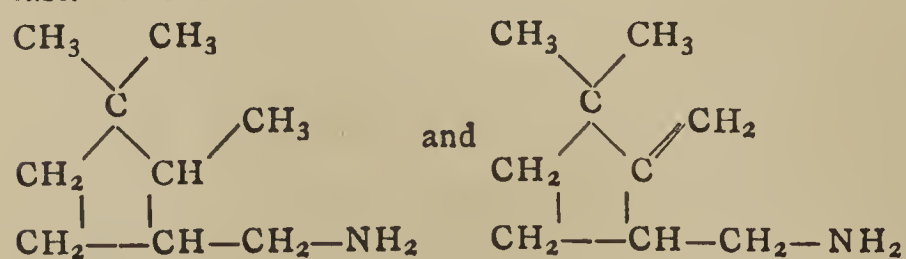
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 2, July 10, 1899.

Tetrachlor-dialcoyl-benzoylbenzoic and Dialcoyl-benzylbenzoic Acids.—A. Haller and H. Umbgrove.—A study of these acids show:—1. They are prepared under identical conditions to those which allow of the preparation of non-chlorated dialcoyl-amido-benzoylbenzoic acids. 2. They differ from the latter in that they are not capable of being directly etherified by ordinary methods, and they do not furnish dialcoyl aniline-phthaleins when they are condensed with dialcoyl-aniline in the presence of acetic anhydride. 3. Under these conditions mixed tetrachlor-acetyl-dialcoyl-benzoylbenzoic anhydrides are formed. 4. These anhydrides, when treated with sodium alcoholate, are transformed into ethers.

Action of Nitrogen Dioxide on the Salts of Chromium Protoxide.—G. Chesneau.—The author's investigations show that chromous salts in solution absorb nitrogen dioxide in the same way as ferrous salts, but they only give a compound containing 1 molecule of N_4O_2 for 3 molecules of the salt. This compound decomposes rapidly, especially if heated or in the presence of acids, but no gas is evolved; the action thus differing from the behaviour of the similar iron salt. The nitrogen of the dioxide is transformed into hydroxylamine or into ammonia, and the oxygen unites with the chromous salt.

Action of Phenylhydrazine on Alcoholic Bromides, Chlorides, and Iodides.—J. Allain de Canu.—The author finds, as he had predicted, that the alcoholic chlorides and bromides do not behave with phenylhydrazine in the same manner as the corresponding iodides. The higher alcoholic iodides also react in a different way from the methyl and ethyl alcoholic iodides.

Amino-campholenes.—E. E. Blaise and G. Blanc.—By treating β -campholenamide with hypobromite of potash, the authors obtain a new base, β -amino-campholene, as a colourless mobile liquid with ammoniacal smell, and boiling at 185° , its density being 0.8778 at 15° . By treating α -campholenamide in the same manner, a new base, α -amino-campholene, is obtained isomeric with the last. The formulæ for the two are:—



An Oxyptomaine.—Æchsner de Coninck.—The author prepares this oxyptomaine by the action of hydrogen peroxide on the pyridic ptomaine, $C_8H_{11}N$. It has

the formula $C_8H_{11}NO$. From this substance are also prepared the bromohydrate, chloraurate, and chloromercurate.

New Method for the Acidimetric Estimation of Alcoloids.—Elie Falières.—Instead of using as an indicator litmus, or any of the ordinary indicators, to estimate the alcoloids, the author employs an ammoniacal copper solution with very good results.

Benzoyl-furfurane.—R. Marquis.—During a research on the subject of the furfuranes the author prepared benzoyl-furfurane. This ketone is easily obtained by acting on benzene with chloride of pyromucyl in the presence of aluminium chloride.

The Egols, New General Antiseptics.—E. Gautrelet.—To prepare these substances, parasulphones obtained from phenols are nitrated, and from this product the orthonitrophenolparasulphonate of mercury and potassium is prepared. The substances thus prepared are called egols—phenegol from phenol, cresegol from cresol, &c. They possess certain antiseptic properties, and they are neither volatile, inflammable, nor explosive.

ERRATUM.—P. 1, col. 1, for "William P. Cutler" read "William P. Cutter."

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S. CHAFFERS, Registrar.

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SESSION 1899-1900.

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Mr. J. G. LORRAIN, M.I.E.E., M.I.M.E., M.S.C.I.,

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NORFOLK HOUSE, NORFOLK STREET, LONDON, W.C.

"PATENTEE'S HANDBOOK" Post Free on application.

THE CHEMICAL NEWS.

VOL. LXXX, No. 273

SOLIDIFICATION OF HYDROGEN.

PROFESSOR DEWAR has succeeded in solidifying hydrogen into a glassy transparent mass.

ON THE ELECTROLYSIS OF THIOSULPHATE OF AMMONIUM.

By P. PIERRON.

It has been recently proposed to introduce hyposulphites into the electrolysis of certain electro-metallurgical operations; it therefore seemed to be of importance to decide what transformations these salts may undergo under the influence of the electric current.

The experiments were carried out on aqueous solutions of thiosulphate of ammonium containing 17.5 per cent of the anhydrous salt. The action at the two poles was examined separately. The solution submitted to electrolysis was contained in a porous pot; a cylindrical platinum electrode was suspended therein; the other electrode, of lead, surrounded the pot, and was plunged into a 10 per cent solution of carbonate of ammonium; when the outer electrode is the anode there would be no inconvenience in replacing this solution by hyposulphite; when, however, it is the cathode, the hyposulphite would give sulphides by reduction, and these would carry HS- or -S- ions into the interior of the pot, and thus complicate the phenomena. The temperature was kept at about 15° by means of a cold-water jacket: platinum was first used as the cathode.

The density of the current at the cathode was from 10, 15, to 40 ampères per decimetre; the phenomenon of reduction always led to the formation of sulphide of ammonium; no other product of this action was detected, and the phenomenon was not examined any closer.

If the inner electrode is the anode the reactions are more complex; we should expect then to form some of the acids of the thionic series; the method of Fordos and Gélis has been applied to their detection. The sulphuric acid formed was estimated in the state of sulphate of barium; an iodometric titration gives the total reducing power of the sulphurous acid and of the unchanged hyposulphite: this treatment with iodine transforms the sulphites into sulphates; a fresh estimation of the sulphuric acid will thus give the proportion of sulphurous acid present; this known, it is easy to deduce from the reducing power the proportion of thiosulphuric acid present. A current of chlorine in alkaline solution transforms all the oxidised compounds of sulphur, with the exception of dithionic acid, into sulphuric acid; this is estimated, and we thus obtain the quantity of sulphur present in the three last thionic acids: finally, by evaporating to dryness, mixing the residue with three times its weight of chlorate of potash, and treating with hydrochloric acid, all the sulphur passes to the state of sulphuric acid; a final titration of this latter gives, by difference, the proportion of dithionic acid. In the experiments we made these two last determinations led to identical results. On the other hand, ammoniacal nitrate of silver is not clouded by the electrolysed ammoniacal solutions, —they hardly colour it brown,—therefore they do not contain pentathionic acid. Under these conditions we can determine the trithionic and tetrathionic acids; the neutral solution is boiled with excess of mercuric cyanide until it is no longer cloudy,

The SO₃H groups contained in the various salts of the solution are thus transformed into sulphates; the remainder of the sulphur is eliminated in the state of sulphide of mercury, or set at liberty. The sulphuric acid is estimated; from the figure found after the deduction of the quantity of sulphuric acid coming from the other acids (sulphuric, sulphurous, hyposulphurous) the quantity of sulphur contained in the thionic acids is deduced. Let P₁ be this weight of sulphur; P₂ the total thionic sulphur: if 3p₃ is the weight of sulphur contained in the existing trithionic acid, 2p₃ will be the weight contained in its SO₃H groupings; in the same way if 4p₄ is the weight of the total tetrathionic sulphur, 2p₄ will be the weight contained in the tetrathionic SO₃H groupings, from whence we obtain the equations—

$$P_1 = 2p_3 + 2p_4, P_2 = 3p_3 + 4p_4,$$

from which we have—

$$p_4 = \frac{P_1 - 2p_3}{2}, \text{ and } p_3 = 2P_1 - P_2.$$

(All these weights are expressed in sulphur). In this manner considerable quantities of tri- and tetra-thionic acids are detected.*

In 200 c.c. of the thiosulphuric solution currents of 28 ampère-hours have been passed at densities of 40, 15, and 3 ampères per square decimetre (the current used was 1.1 ampère), at a temperature of from 12 to 16°. From the commencement and during the whole time sulphur is deposited, and sulphurous anhydride given off; in an experiment at 40 ampères density this sulphur adhered strongly to the platinum, increased the resistance of contact, and caused a decided elevation of temperature of the electrode; the conditions of the experiment were thus slightly different from those of the other experiments. In all three cases the electrolyte became acid.

The method of analysis described above gave the following results:—

Density at the the anode.	40 ampères per decim.	15 ampères.	3 ampères.
S deposited ..	15.20	9.62	5.16
S sulphuric ..	7.20	5.92	5.32
S sulphurous ..	1.21	1.30	1.07
S trithionic ..	2.81	1.35	2.87
S tetrathionic .	3.99	5.70	8.71

From these figures we get the increase of the deposit of sulphur and of the quantity of sulphuric acid with the density of the current, and the simultaneous diminution of the tetrathionic acid. The proportion of sulphurous acid remains practically constant; that of trithionic acid shows a variation which is not easy to explain by reason of the complexity of the phenomena; as to its presence, it was foreseen from the work of Plessy and Rathke: the hyposulphite is here found in the presence of sulphurous acid and of acid sulphite. It is easy to understand, on the other hand, the inverse variation of the quantities of tetrathionic acid, sulphuric acid, and deposited sulphur. The tetrathionic acid evidently here results from oxidation, and not from addition, as, for example, persulphuric acid; the diminution of returns at high current densities proves this, and, further, for this addition to be possible it would be necessary for the sulphydric atoms, -S- (SO₃H), to take a prominent part in the electrolysis, and be consequently more easily dissociated than the other, which is extremely probable in the concentrated solution submitted to electrolysis. At the commencement, then, of the electrolysis some of the ions -SO₃.S.NH₄ are set at liberty, and split up into sulphur, sulphurous acid, and sulphate of ammonia:—



This latter immediately takes part in the electrolysis,

* P might be measured by determining the total alkali, after exactly neutralising the solution. In fact ammonium, NH₄, corresponds in the series to an SO₃H grouping.

forming sulphuric acid, which makes the solution acid, and oxygen, which transforms the thiosulphate into tetrathionate. If the surface of the electrode is large, at the end of a few moments the sulphate is electrolysed almost alone, being the most easily dissociated of the salts in solution, and the phenomenon of oxidation to tetrathionate goes on. If the surface is small, the electrolyte in its neighbourhood will become poor in sulphuric ions and the thiosulphate will continue to be electrolysed, giving sulphate, sulphur, and sulphurous acid; the return of tetrathionate, which is in direct relation with the quantity of sulphuric ions given off, diminishes accordingly. Besides these phenomena, an oxidation of sulphurous acid takes place, and possibly an oxidation of the thionic acids which does not allow of uniformity between the two sets of reactions: what leads to this last supposition is, that in the electrolysed solutions we do not find either pentathionic acid or sulphuretted hydrogen, which ought to be present as products of the decomposition of the hyposulphite under the slow influence of the sulphuric acid set at liberty. Small quantities of the former have been detected in the early part of the electrolysis, but they gradually disappear. It is thus evident that these bodies are destroyed during their formation by the oxidising action of the surrounding material, and the other thionic acids—although having greater resistance—should be equally destroyed. These products of the destruction of the hyposulphite are evidently oxidised at the expense of forming tetrathionate; by checking the acidity of the solution by adding ammonia during the electrolysis, we could diminish the formation of tetrathionate, and the deposit of sulphur, and the formation of sulphuric acid; experiment has confirmed this view. But the experiments made in this direction were not sufficiently exact to give very good results.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 10.

THE PLACE OF THE NEW CONSTITUENTS OF THE ATMOSPHERE IN THE PERIODIC SYSTEM.

By JAS. LEWIS HOWE.

FROM the first announcement of the discovery of argon, the interest of chemists has been engaged as to what place the element would occupy in the periodic system, and this interest has increased as the efforts of Ramsay have brought to light other closely related elements of the same nature—helium, neon, krypton, metargon, and xenon. By some it has been held that it is impossible to find a place in the system for these elements; by others, that they can be easily located. Piccini, in the *Zeitschrift für Anorganische Chemie* (xix., 295), has recently given an excellent review of the more important of these opinions. It is the purpose of this paper to consider several of the arguments on the subject.

One of the arguments which has been adduced by those who hold that the periodic system is inconsistent with the existence of these elements, is that the atomic weight of argon is apparently greater than that of potassium, and there is no place in the periodic table for an element between potassium and calcium. While there is room for it between chlorine and potassium, its atomic weight would not allow it to be placed here. This objection to the periodic table is by no means unique, for it applies equally well to cobalt and tellurium. The latest and best atomic weight determinations give cobalt a higher atomic weight than nickel, and tellurium a higher atomic weight than iodine. According to the table of Mendeleeff or of L. Meyer the reverse should be the case. The real difficulty, however, does not rest with the table. In its properties cobalt lies clearly between iron and nickel, to as great a degree as rhodium lies between ruthenium and palladium, and cobalt is undoubtedly the analogue of rhodium. Similarly, as far as investigated,

the properties of tellurium seem to be between those of antimony and iodine, even as those of selenium are between those of arsenic and bromine, and, in spite of some efforts to the contrary, tellurium must be considered as the analogue of selenium, and a member of Group VI. The apparent inconsistencies in these cases rest with the facts, and the table merely reveals them. If it be true that an element lying between two others in respect of atomic weight must possess intermediate properties, then it is the atomic weight determinations which are at fault. This may indeed be the case, and, if so, errors are certainly no less probable in the case of argon than in case of cobalt, nickel, and tellurium; but if it should prove, as now seems probable, that the atomic weights in question are approximately and relatively correct, then it must follow that an element need not in every case have an atomic weight intermediate between the two elements, between which it lies in respect of properties,—that is, it may pass slightly outside of these limits. This fact would be expressed in the periodic table by an element occasionally having an atomic weight slightly greater than that of the element which follows it; but the law upon which the periodic system is based, that the properties of elements are a periodic function of their atomic weights, would still be true. We may express this idea mathematically by the equation—

$$\text{Atomic weight} = \phi(n) + \psi(m),$$

where ϕ is relatively large and simple and ψ relatively small and complex. Here, while in general the atomic weight will increase as n increases, it is possible that for certain values $\psi(m)$ may have sufficient weight to cause the atomic weight to retrograde temporarily: this would be expressed in the periodic table by certain elements having slightly higher atomic weights than the element which follows them. It is by no means impossible that the anomalous atomic weights of cobalt (or nickel) and tellurium may be accounted for in this way, and if argon should come into the same category it would throw no discredit upon the periodic system.

The question is raised by Piccini as to whether the periodic system of Mendeleeff is open to the reception of elements of which no compounds are known, and this he answers in the negative. Now if the properties of the elements are a periodic function of their atomic weights, and this is in general acknowledged by most chemists, then it must follow that the properties of argon, neon, and helium are functions of their atomic weights, or else argon, neon, and helium are not chemical elements in our ordinary sense of the term. The periodic table, as heretofore said, merely expresses in a visible, easily comprehensible way the fact of the law. It is for us, then, to consider as to whether argon, neon, and helium can find a place in this table.

Now in the table as given by Mendeleeff, as well as in that of L. Meyer, it is not clear that there is a natural place for these elements; indeed there has always been in these tables a difficulty in the relations between the short and the long periods, and especially with the eighth group, in which these new atmospheric elements fall. This Group VIII. has been a sort of catch-all into which iron, cobalt, nickel, and the platinum metals have been dumped, with little attempt at order or consideration of their properties. They are a manifest irregularity in the tables, and the tables would be as well or even better off did these metals not exist. As a matter of fact, however, this Group VIII. plays a very important part if the table is arranged on an upright cylinder, in the form adopted by L. Meyer in the third edition of his "*Moderne Theorie der Chemie*." Here it is clearly seen that Group VIII. is as much a transition group, for three periods, from Group VII. to Group I., as Group IV. is a transition group from III. to V. The relations of the new elements is most clearly seen by means of the subjoined table, which is practically that of Venable. While Venable's table was first proposed merely as a convenient form for teaching,

M_2O		MO		M_2O_3		MO_2 H_4M		M_2O_5 H_3M		MO_3 H_2M		M_2O_7 HM							
H (?)														He					
Li		Gl		B		C		N		O		F		Ne					
Na		Mg		Al		Si		P		S		Cl		Ar					
K		Ca		Sc		Ti		V		Cr		Mn		Fe		Co		Ni	
Cu		Zn		Ga		Ge		As		Se		Br		[82]		[84]			
Rb		Sr		Y		Zr		Cb		Mo		—		Ru		Rh		Pd	
Ag		Cd		In		Sn		Sb		Te		I							
Cs		Ba		La		Ce		*		*		*		*		*		*	
†		†		†		†		†		†		†							
*		*		*		*		Ta		W		*		Os		Ir		Pt	
Au		Hg		Tl		Pb		Bi				†		†					
*		*		*		Th		*		U									
+ Series.		- Series.		+		-		+		-		+		-					

* Possible + series elements.

† Possible — series elements.

— Ekamanganese.

it deserves far wider recognition, as it brings out the natural relations of the elements in many respects more clearly than any other form of table, and at the same time avoids certain difficulties which appear in other tables, especially that regarding the short and long periods. The table here given differs from that of Venable chiefly in leaving places for possible elements with atomic weights greater than 140, and in placing helium, neon, and argon in what appears to be their natural position.

Here the three new elements appear clearly as transition elements between the halogens and the alkalis, except that there is no halogen of lower weight than fluorine. Is this position justifiable? The arguments in its favour are not new, but may be here repeated for emphasis.

a. Elements with no chemical affinity would be a natural transition from the strongly negative halogens to the strongly positive alkali metals.

b. The valence toward hydrogen being in Group IV. four, in Group V. three, in Group VI. two, and Group VII. one, would naturally in Group VIII. be zero, which expresses the fact that these elements form no compound with hydrogen.

c. Towards oxygen and other negative elements we have, in Groups IV., III., II., I., respectively a valence of four, three, two, one; in Group VIII. we should then expect a valence of zero, and this is expressed by the fact that the new elements form no compounds with negative elements, as far as experiment has yet shown.

It is not inconceivable that these elements might have even a valence of eight toward oxygen, following the analogy of the halogens with a valence of seven; but valence is greatly modified by electro-chemical character, as is shown by the fact that, while from its position a compound Fl_2O_7 might be expected, fluorine—owing to its

electro-chemical character—forms no compound at all with oxygen.

The question, however, arises at once regarding the nine metals of Group VIII., if the above arrangement holds good. To explain this we must consider Venable's table. To the elements of the first period (lithium—fluorine) he gives the name of *group* or *bridge elements*; to those of the second period (sodium—chlorine) *type elements*, as *they*, rather than the *group elements*, foreshadow the character of the succeeding elements of the respective groups. After the type element each group divides into two series, a positive and a negative, as shown in the table. Now the Group VIII. metals mark the transition from the positive series of the Group VII. to the negative series of Group I. Now since the electro-chemical character of manganese differs little from that of copper, and that of eka-manganese would differ little from that of silver, we have in these cases a gradual transition through iron, cobalt, and nickel, respectively ruthenium, rhodium, and palladium. Manganese and copper both form compounds with oxygen and chlorine in which the positive elements are bivalent, and we find the same true of iron, cobalt, and nickel. Manganese acts also with higher valences toward oxygen, and we find the same true with iron, cobalt, and nickel, iron approaching manganese most closely in this respect, and cobalt next. An analogous line of argument applies to the ruthenium group and to the osmium group. Argon, on the other hand, is a transition element from the type element (negative) chlorine of the most strongly negative Group VII. to the positive series of the most strongly positive Group I.

There seems, however, at first sight, to be a decided inconsistency in placing these inert elements—helium, neon, and argon—in the same group with iron, cobalt, nickel, and the platinum metals. From its position argon would seem to be the *type element*, but the metals of this group in no way resemble it. We notice from the table that in Group I. the elements of the positive series very closely resemble the type element, sodium. In Group II. the positive series elements resemble magnesium, but not quite so closely. This resemblance of the elements of the positive series to the type element decreases continuously until in Group VII., the least positive group, the only element of the positive series, manganese, bears very little resemblance to the type element, chlorine. In Group VIII. it is, then, not unexpected that this resemblance wholly disappears, and we find no similarity between iron, cobalt, nickel, and the platinum metals on the one hand, and argon on the other.

Proceeding in the reverse direction, the change differs only in degree. In Group VII., the most negative group, the elements of the negative series, bromine and iodine, very closely resemble the type element chlorine, and this resemblance decreases continuously until in Group I., the least negative group, the elements of the negative series differ very decidedly from the type element sodium. In Group VIII. all resemblance disappears. There is therefore nothing inconsistent with this location of the new elements in Group VIII. of the periodic table.

One other point tells strongly in favour of the view that helium, neon, and argon are true elements, which is implicitly brought out by Ramsay in his recent address before the Deutscher Chemischen Gesellschaft. The first natural relation which was discovered between the chemical elements was Döbereiner's *law of triads*, and it was this idea which led Ramsay to that wonderfully painstaking and happily successful search for neon. Like so many other groups of elements, the three elements helium, neon, and argon agree with the relations pointed out so long ago by Döbereiner, and this indicates that the elemental nature of these gases is not different from that of the other elements.

A few words may be said in conclusion regarding the other gases which Ramsay met in his search for neon, *i.e.*, krypton, metargon, and xenon. Too little is yet known of them to render it possible to locate them in the periodic

table; but it can readily be seen that there is sufficient space for them in the Group VIII., should their atomic weights so indicate. Whether Group VIII. itself should not be split up into three distinct groups is an open question. Certain it is that in many respects the three triads—iron, ruthenium, and osmium; cobalt, rhodium, and iridium; nickel, palladium, and platinum—differ from each other in no small degree, perhaps sufficiently to deserve to be placed in three distinct groups. If this be the case, it may be that there would be a group element and a type element for each group, as well as elements corresponding to the copper-bromine period, and perhaps to the higher missing periods. Or, on the other hand, two transition elements might occur between bromine and rubidium, of atomic weight of about 82 and 84 respectively, taking their place between the iron, cobalt, and nickel triads; corresponding to these would be two type elements for Group VIII., of which metargon might be one. This is of course mere speculation, but it serves to show that there is room not only for helium, neon, and argon in this Group VIII., but also for other elements of similar properties, and this without doing violence to the periodic law, which must be considered as the greatest generalisation of modern chemistry.

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ON A TEST,
BY THE FREEZING-POINT METHOD,
OF THE
IONISATION COEFFICIENTS DETERMINED BY
THE CONDUCTIVITY METHOD,
FOR
SOLUTIONS CONTAINING POTASSIUM AND
SODIUM SULPHATES.*

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(Concluded from p. 69).

Depression of the Freezing-point by the Mixtures.

THE accompanying table contains the observed and calculated values of the depression of the freezing-point in the case of the mixtures examined. The observations were made in the manner described above. The calculations were made by the following formula, for which I am indebted to Professor MacGregor:—

$$\Delta = 1.86 (1 + a_1 + a_2) N/2;$$

where a_1 and a_2 are the ionisation coefficients of the respective electrolytes in the mixture and N the number of grm.-equivalents per litre in the solutions mixed, which were in all cases equimolecular. This expression may be readily obtained as follows:—In each litre of the mixture there will be $N/4$ grm.-molecules of each electrolyte. There will therefore be $(1 - a_1) N/4$ and $(1 - a_2) N/4$ undissociated grm.-molecules of the respective electrolytes, and, if we assume the ionisation in each case to be complete, $3 a_1 N/4$ and $3 a_2 N/4$ free grm.-ions. Hence the total number of undissociated grm.-molecules and free grm.-ions will be $(1 + a_1 + a_2) N/2$, and the expression for the depression will consequently be as above.

The first column of Table V. gives the concentration of the solutions mixed, in grm.-equivalents of anhydrous salt per litre at 18° C. The fifth and sixth columns give the ionisation coefficients of the respective electrolytes in the mixture at 0° C. as determined by Prof. MacGregor's method. The second, third, and fourth give the quantities obtained directly by this method, *viz.*, the common concentration of ions, and the dilutions of the respective electrolytes in the mixture. (By the concentration of ions

* From the *Transactions of the Nova Scotian Institute of Science*, vol. x., Session 1898-99.

TABLE V.

Concentration of constituent solutions at 18° C. (grm.-equiv. per litre).	Concentration of ions in mixture at 0° C.	Dilution in mixture at 0° C.		Ionisation coefficients in mixture at 0° C.		Depression of freezing-point.		
		$\frac{1}{2}$ K ₂ SO ₄ .	$\frac{1}{2}$ Na ₂ SO ₄ .	K ₂ SO ₄ .	Na ₂ SO ₄ .	Observed.	Calculated.	Diff. per cent.
0.050	0.0377	20.04	19.96	0.7555	0.7525	0.1187	0.1166	-1.8
0.055	0.0410	18.22	18.14	0.7470	0.7437	0.1299	0.1274	-1.9
0.060	0.0443	16.72	16.60	0.7407	0.7354	0.1411	0.1382	-2.1
0.070	0.0509	14.40	14.18	0.7330	0.7218	0.1634	0.1598	-2.2
0.080	0.0574	12.60	12.40	0.7232	0.7118	0.1854	0.1812	-2.3
0.100	0.0698	10.18	9.92	0.7106	0.6924	0.2284	0.2235	-2.1
0.150	0.0998	6.73	6.60	0.6717	0.6587	0.3327	0.3250	-2.3
0.200	0.1266	5.10	4.90	0.6457	0.6203	0.4321	0.4215	-2.5
0.250	0.1528	4.10	3.90	0.6265	0.5959	0.5295	0.5166	-2.4
0.300	0.1784	3.46	3.21	0.6173	0.5727	0.6246	0.6110	-2.2
0.400	0.228	2.63	2.37	0.5996	0.544	0.8096	0.7961	-1.7
0.500	0.227	2.12	1.88	0.5872	0.528	0.9885	0.9802	-0.8
0.600	0.327	1.79	1.54	0.5853	0.5036	1.1654	1.1657	+0.5
0.700	0.376	1.54	1.31	0.5790	0.4926	1.3300	1.3489	+1.4

in the mixture is meant the number of dissociated grm.-equivalents of either electrolyte in any volume of the mixture divided by the volume of that portion of the mixture which may be regarded as occupied by it. The dilutions of the electrolytes in the mixture are the volumes of such portions divided by the number of grm.-equivalents of the electrolytes they contain. The product of these two quantities for each electrolyte gives the ionisation coefficient of such electrolyte in the mixture). The data of the other columns are sufficiently specified by the headings.

If we compare the percentage differences of Table V. with the corresponding differences in the case of the constituent simple solutions (Table IV.), it will be seen that the former are in general equal to the arithmetic means of the latter. Hence the depressions of the freezing-point of the mixtures have been calculated with the same degree of accuracy as those of the simple solutions.

The test which has thus been applied to Professor MacGregor's method of determining the ionisation coefficients in a solution containing two electrolytes with a common ion, and which the method has completely satisfied, is, however, not a severe one. It was intended, after the experiments on equimolecular solutions, to take up mixtures of solutions of different concentrations with respect to the two electrolytes. Unfortunately, I was prevented from doing so by lack of time.

In conclusion, I wish to express my thanks to Prof. MacGregor for valuable suggestions kindly given.

THE PHYSIOLOGICAL EFFECT OF CREATIN AND CREATININ, AND THEIR VALUE AS NUTRIENTS.*

By J. W. MALLETT, M.D., LL.D.,
Professor of Chemistry in the University of Virginia.

(Concluded from p. 71).

Conclusions.

THE main conclusion to be drawn is manifestly this:—That by far the larger part of the flesh bases ingested, if not absolutely the whole, does not undergo metabolism with the production of urea or anything else, but, on the contrary, is eliminated by way of the kidneys. In the case of creatinin it is excreted unchanged, while creatin is changed wholly or very largely into creatinin.

This elimination in the urine of the flesh bases is reflected in the figures giving the specific gravity of the excretion. Two experiments only were made with a view to ascertaining whether any of the creatin or creatinin

taken in heavy doses could be recovered from the aqueous extract of the faeces, it seeming possible that the comparatively slight solubility of creatin in particular might lead to some of it escaping absorption along the course of the intestinal canal. In these two cases the results were altogether negative.

The fact of the quantitative recovery of creatin and creatinin from the urine evidently accords fully with the generally accepted belief that these substances cannot serve to build up proteids, and therefore are not to be classed among tissue-forming food materials.

On the whole, this investigation is unfavourable to the idea of the creatin of living muscle being the main antecedent of urea in nitrogenous metabolism. It is, of course, conceivable that the creatin of the living muscles may be slowly metabolised with production of urea, and that, as Voit has remarked, the cause of the ingested flesh bases appearing in large amount in the urine, instead of undergoing conversion into urea, may be that time enough has not been allowed for metabolism, but this is rendered very improbable by the large quantity of urea given off daily. It can hardly be admitted that such slow and difficult formation of urea from creatin can possibly represent the regular course of change by which the bulk of the urea is produced. It must be remembered, of course, that creatin swallowed, as in the above experiments, and getting into the blood by absorption from the alimentary canal, does not follow exactly the same course and is not placed under exactly the same conditions as that found in and derived from the living muscles. However, it is not easy to imagine such a difference in the fate of the same substance from these two sources, once having become a constituent of the blood, as would account for its being in the one case metabolised and in the other eliminated unchanged or merely converted into its anhydride, creatinin.

However this may be, and admitting that it is still an unsolved problem, what nitrogenous substance or substances may properly be regarded as intermediate between muscle proteids and urea, it may fairly be regarded as established for nutrition investigations that the so-called flesh bases, creatin and creatinin, occurring in food may be entirely disregarded as sources of energy, being excreted practically without having undergone change.

This conclusion seems to be deserving of attention—on the one hand, by the analyst of food materials, and, on the other by the physician who prescribes and the consumer who makes use of the ordinary meat extracts.

In the discussion of the results of analyses of meat and forms of food prepared from it, such as soups and the like, it is evidently wrong and misleading to confound together, under the head of protein or proteid materials, the proteids proper, capable of building up the nitrogenous tissues of the living body and of furnishing muscular energy and heat by oxidation, and these so-called flesh

* Bulletin, No. 66, United States Department of Agriculture, Office of Experiment Stations.

bases, which, taken in along with food, are not available for either of these important purposes. This error is the more serious that creatin and creatinin, containing so large a percentage of nitrogen as they do, appear to represent and are counted as representing much more than their own weight of nutrient material, whereas they should be excluded altogether in food analyses from the nutrient material really present.

As regards the practical use of meat extracts, those forms of such preparations from which the proteids and peptones have been removed, may well be considered as destitute of nutritive value, and those in which, along with some proteid material, the flesh bases occur in large quantity may be considered as deriving no nutritive value from this latter source.

Even if viewed in the light of nerve stimulants only, and thus to be classed with tea and coffee as adjuncts to food rather than as true food itself, meat extracts, so far as the flesh bases creatin and creatinin are concerned, are shown by this investigation to be very much less active in their effects upon the nervous system than they have been commonly reputed. The potassium salts present in large quantity in meat extracts, are by no means to be overlooked as influencing such effects as are produced upon the living organism, and it may be that some of the minor organic constituents are relatively more potent than creatin and creatinin, but aside from such real proteid or peptonic material as is in some cases present, the meat extract preparations may fairly be relegated on the whole to the class of condiments or flavouring matters rather than to that of foods or medicines.

Suggestions for Further Investigations.

It is desirable that the following points suggested by this investigation should, if possible, be examined. To this end it might be desirable—

1. By experiments, with other persons as subjects, to ascertain the influence, if any, of age, sex, &c., upon the behaviour of the flesh bases in the living organism.
2. To try the effect of a given amount of creatin or creatinin, administered at once as a single dose, as compared with the same quantity divided into several parts, administered as separate doses, and distributed over several hours with but short intervals.
3. To try to recover creatin or creatinin (administered by the mouth) from the blood of one of the lower animals killed or heavily bled soon after receiving a large dose of the flesh base. This would involve the interesting question whether creatinin can undergo conversion into creatin in the alkaline blood and such reaction be afterwards reversed in connection with elimination by the kidneys.
4. To examine, not the whole urinary excretion of twenty-four hours, but several samples of urine taken at short successive intervals for two or three hours after the ingestion, by swallowing, of a large dose of creatin or creatinin, so as to get a more definite idea of the rapidity with which elimination takes place, to obtain further evidence as to creatin being capable of passing through the renal filter without conversion into creatinin, and to see whether the reverse change can occur.
5. To examine more fully the observed reversal of the normal acid reaction of the urine after ingestion of a large amount of creatin.

Metallic Sulphantimonites. — M. Pouget. — The action of metallic salts on a solution of sulphantimonite of potassium gives, by double decomposition:—1. A trimetallic sulphantimonite, SbS_3M_3 . 2. A double sulphantimonite, $\text{SbS}_3\text{M}_2\text{K}$. (In no case was the author able to prepare the monometallic salt, SbS_3MK_2). The double decomposition is sometimes accompanied by a reduction. Solutions of orthosulphantimonites of sodium and lithium give similar results.—*Comptes Rendus*, cxxix., No. 2.

THE TITRATION OF OXALIC ACID BY POTASSIUM PERMANGANATE IN PRESENCE OF HYDROCHLORIC ACID.*

By F. A. GOOCH and C. A. PETERS.

LÖWENTHAL and Lenssen (*Zeit. Anal. Chem.*, i., 329) were the first to show that the titration of a ferrous salt by potassium permanganate in the presence of hydrochloric acid, according to the process of Margueritte (*Ann. de Chim. et de Phys.*, [3], xviii., 244) is vitiated by the evolution of chlorine outside the main reaction, and to point out that a remedy for the difficulty is to be found in the titration of the ferrous salt in divided portions, other equal volumes of the ferrous solution being added to the liquid in which the first titration is accomplished until the amount of iron indicated by successive titrations becomes constant.

Kessler (*Ann. d. Phys. u. Chem.*, cxviii., 48; cxix., 225) showed the restraining influence of certain sulphates, of manganous sulphate in particular, upon the irregular and undesirable interaction of the permanganate and hydrochloric acid; and Zimmermann (*Ann. d. Chem.*, ccxiii., 302), in apparent ignorance of Kessler's forgotten proposal, advocated the introduction of a manganous salt, best the sulphate, into the ferrous salt to be determined, thus accomplishing the purpose of the empirical procedure of Löwenthal and Lenssen.

The tendency toward evolution of chlorine in the oxidation of a ferrous salt by permanganate, as compared with the absence of such tendency in the similar oxidation of oxalic acid, in presence of hydrochloric acid, was explained by Zimmermann on the hypothesis that an oxide of iron higher than ferric oxide is formed as an intermediate product, and that this unstable oxide is sufficiently active to break up hydrochloric acid as well as to oxidise more of the ferrous salt. Quite recently, Wagner ("Maasanalytische Studien, Habilitationsschrift," Leipzig, 1898) finds explanation of the sensitiveness of the hydrochloric acid solution of the ferrous salt in the probable formation of chlor-ferrous acid (analogous to chlor-platinic and chlor-auric acids), which suffers oxidation more readily than hydrochloric acid under the action of the permanganate. The protective influence of the manganous salt turns apparently, as Zimmermann suggested, upon the initiation of Guyard's reaction, according to which the permanganate and manganous salt interact to form a higher oxide of manganese of a constitution approaching the dioxide more or less closely—this oxide being capable of oxidising the ferrous salt, but slow to act upon the hydrochloric acid or the chlor-ferrous acid of Wagner. According to Volhard (*Ann. d. Chem.*, 1879, cxcviii., 318), the reaction of Guyard is favoured and hastened by heat and concentration of the solution, while it is delayed by acidity and dilution; but even in solutions containing very little manganous salt and a considerable quantity of free acid the faint rose colour developed by the careful addition of permanganate ultimately vanishes until every trace of the manganous salt is precipitated. When a considerable amount of the salt is present, interaction follows immediately the introduction of the permanganate. Zimmermann advocates the use of 4 grms. of manganous sulphate uniformly in titrations of a ferrous salt by permanganate—a procedure to which Wagner gives acquiescence, though pointing out that a ninth of that amount is all that he finds to be necessary. The excess of the manganous salt can do no harm so long as the higher oxide, the product of interaction of the manganous salt and the permanganate, is immediately reduced by even traces of a ferrous salt, and this appears to be the case at least within the limits proposed by Zimmermann and Wagner. Thus we

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, Fourth Series, vol. vii., June, 1899.

TABLE I.

Total volume at beginning of titration. C.m. ³ .	HCl. Sp. gr. 1.09. C.m. ³ .	FeCl ₂ C.m. ³ .	KMnO ₄ . 1/10 N. C.m. ³ .	MnSO ₄ .5H ₂ O. Grms.	MnCl ₂ .4H ₂ O. Grms.
135	10	25	21.70	1	—
135	10	25	21.70	3	—
135	10	25	21.70	5	—
135	10	25	21.75	7	—
135	10	25	21.75	10	—
145	20	25	21.75	10	—
175	50	25	21.75	10	—
135	10	25	21.70	—	1
135	10	25	21.70	—	2
145	20	25	21.70	—	2
155	30	25	21.75	—	3
165	40	25	21.70	—	4

TABLE II.

(Temperature at beginning about 80° C.).

Approximate volume at beginning of titration.	H ₂ SO ₄ . 1:1. C.m. ³ .	HCl. Sp. gr. 1.09. C.m. ³ .	Ammonium oxalate. 1/10 N. C.m. ³ .	KMnO ₄ . C.m. ³ .	Variation from mean of A taken as standard. C.m. ³ .
A					
200	5	—	50	47.50	0.00
200	5	—	50	47.50	0.00
200	10	—	50	47.50	0.00
200	10	—	50	47.50	0.00
200	25	—	50	47.50	0.00
200	25	—	50	47.50	0.00
B					
150	10	2.5	25	23.80	+0.05
150	10	2.5	25	23.90	+0.15
150	10	5.0	25	23.90	+0.15
150	10	10.0	25	24.00	+0.25
500	5	—	25	23.80	+0.05
500	10	10.0	25	24.00	+0.25
500	10	10.0	25	24.10	+0.35

TABLE III.

(Temperature at beginning about 80° C.).

Volume at beginning. C.m. ³ .	H ₂ SO ₄ . 1:1. C.m. ³ .	Ammonium oxalate. 1/10 N. C.m. ³ .	MnSO ₄ .5H ₂ O. Grms.	KMnO ₄ . C.m. ³ .	Variation from standard.
130	5	25	—	23.75	0.00
130	5	25	0.0008	23.75	0.00
130	5	25	0.0032	23.75	0.00
130	5	25	0.0160	23.75	0.00
130	5	25	1	23.70	-0.05
130	5	25	2	23.75	0.00
130	5	25	2.5	23.60	-0.15
130	5	25	3.0	23.40	-0.25
130	5	25	4.0	23.60	-0.15
500	5	25	—	23.80	+0.05
500	5	25	0.0008	23.80	+0.05
500	5	25	0.0032	23.80	+0.05
500	5	25	1	23.70	-0.05
500	5	25	2	23.40	-0.35
500	5	25	3	23.50	-0.25
500	5	25	4	23.30	-0.45
130	10	25	1	23.80	+0.05
130	10	25	2	23.75	0.00
130	10	25	3	23.65	-0.10
130	10	25	4	23.50	-0.25
130	15	25	2	23.75	0.00
130	15	25	4	23.70	-0.05
130	15	25	5	23.50	-0.25
130	30	25	2	23.75	0.00
130	30	25	4	23.70	-0.05
130	30	25	5	23.75	0.00

find, as shown in results of Table I., that so much as 5 grms. of the sulphate may be present in 135 c.m.³ of the liquid containing about 5 c.m.³ of hydrochloric acid of full strength, without interfering with the regularity of the titration; and the effect is trivial even when the amount of manganous sulphate reaches 10 grms. We find, also, practical regularity of working when manganous chloride is substituted for the sulphate, and in this

respect our results accord with those of Zimmermann and differ from those of Wagner (*loc. cit.*, p. 104).

In all cases, however, in which the larger amounts of manganous salt are present, the end-reaction is marked by the advent of a brownish red precipitate rather than the clear pink of the soluble permanganate, and it is obvious that in case the solutions to be oxidised were not active enough to act with rapidity upon the product of the Guyard reaction, difficulty might follow the failure to adjust the conditions more particularly.

It has been stated by Fleischer ("Volumetric Analysis," trans. by Muir, p. 71) and Zimmermann (*loc. cit.*) that hydrochloric acid interferes in no way with the titration of oxalic acid by potassium permanganate. This statement, however, is not in accord with our experience; for we find that in such titrations there is a small though real waste of permanganate proportionate to the amount of hydrochloric acid present. This fact is brought out clearly in the comparison of experiments of Section A (Table II.), in which no hydrochloric acid was present, with experiments B, in which hydrochloric acid was present.

From these results it is evident that, though the error introduced by the presence of the hydrochloric acid during the action of the permanganate upon the oxalic acid is small, it is plainly appreciable. The questions arise, therefore, first, as to whether the secondary action of the permanganate upon the hydrochloric acid may be prevented by the presence of a suitable amount of a manganous salt: and, secondly, as to whether in this event the reducing agent—the oxalic acid—is sufficiently active, like the ferrous salt, to prevent the premature establishment of an end colour due to the Guyard reaction. The latter question must naturally be settled before the former can be taken up. In Table III. are recorded the effects of varying amounts of manganous salt in presence of different amounts of sulphuric acid in the reaction of permanganate upon oxalic acid.

From the results given it is evident that the persistence of the Guyard reaction is liable to interfere with the end-reaction of oxidation of oxalic acid unless an adjustment is made between the quantity of the manganous salt, the amount of acid, and the dilution. In hot solutions of a total volume of 130 c.m.³ at the beginning, no more than 2 grms. of the manganous sulphate should accompany 5 to 10 c.m.³ of the 1:1 sulphuric acid; when the total volume at the beginning reaches 500 c.m.³, no more than a single gm. of the salt should be present with 5 c.m.³ of the 1:1 sulphuric acid. The amount of manganous salt may, however, be increased considerably if the quantity of acid is increased.

(To be continued).

Researches on Argon and its Combinations.—M. Berthelot. — The author, having obtained from Prof. Ramsay a large quantity of argon, repeated his former experiments on the reaction between argon and certain metallic compounds. Negative results were obtained when argon was mixed with ethylene, glycollic ether, aldehyde, acetone, amylene petroleum ether, propionitrile, allyl sulphocyanide, or amylamine, and the mixture subjected for some time to the action of the silent electric discharge. In all these cases the original volume of argon was recovered unchanged. In the case of mixtures of benzene, toluene, cymol, turpentine, anisol, phenol-benzaldehyde, aniline, phenyl sulphocyanide, or benzonitrile with argon, being subjected to the same treatment, argon was absorbed to the extent of 1 to 6 per cent of the total volume. At the same time a greenish fluorescence appeared, giving a characteristic spectrum. — *Comptes Rendus*, cxxix., No. 2.

ON THE CLAIMS OF DAVYUM TO RECOGNITION AS A CHEMICAL ELEMENT.*

By J. W. MALLETT.

IN the year 1877 the Russian chemist, Sergius Kern, announced (*Compt. Rend.*, lxxxv., 72; *CHEM. NEWS*, xxxvi., 4, 114, 155, 164, and xxxvii., 65) that in treating native platinum ore he had detected a new metal of the platinum group, which he proposed to name in honour of Sir Humphry Davy. A brief description was given of the process by which the separation of the metal was effected, and some of its reactions were described. The metal itself was said to be silvery in appearance, fusible with difficulty by means of the oxy-hydrogen blowpipe, hard, and to some extent ductile, of sp. gr. 9.385 at 25° C. Only 0.27 gm. was obtained from 600 grms. of the platinum ore, = 0.045 per cent., and in subsequent papers the author spoke of it as still more sparingly obtainable, saying that most of the platinum ore used contained but 0.0008—0.001 per cent, that only a few samples gave as much as 0.035—0.045 per cent, and that the whole quantity of davyum obtained was "so small that no serious experiments could be made." The only report by another chemist on the existence of this claimant for distinct elementary character seems to be a very short paragraph in Valentin's "Course of Qualitative Chemical Analysis" (6th edition, 1884), in which the editor, Dr. W. R. Hodgkinson, says that he has obtained a small quantity of the new metal from native platinum, and has found that "it decomposes water in presence of H₂SO₄, the oxide formed scarcely dissolving in the acid"—a very remarkable statement in regard to a metal of the platinum group.

Most compilers of chemical handbooks have either ignored davyum altogether, or have relegated it to mere mention among the sundry "supposed elements," of which the list is not a short one. It is desirable that this list be as far as possible expurgated, and any experiments tending to establish or overthrow belief in the existence of a supposed element have some interest.

The point which seems to make it particularly interesting to decide whether there is such a metal as davyum or not, is the statement by Kern that the atomic mass, as determined in preliminary experiments by Alexejeff, must be near to 154. This would suggest the possible existence in the "periodic" classification of the elements of a hitherto unrecognised element, or more probably a triad of elements, analogous to the triads—ruthenium, rhodium, palladium, and osmium, iridium, platinum—and having an average atomic mass about half way between these two sets of three. Thus we should have:—

Ruthenium	100.91	?	Osmium	189.55
Rhodium..	102.23	Davyum 154?	Iridium..	191.66
Palladium	105.56	?	Platinum	193.41

It is noteworthy that in Mendeleeff's arrangement of the elements in groups and series, we have representatives of the eighth group in the fourth, sixth, and tenth series, but none in the eighth series, a place which would be taken by elements with atomic masses approximately equal to that attributed to davyum. So that, if the existence of davyum were established, it would render probable the subsequent discovery of two more metals analogous to it.

As the best means of securing a favourable chance for investigating the existence or non-existence of the supposed element, I wrote two or three years ago to Mr. George Matthey, F.R.S., of London, knowing the generous readiness to aid scientific research which he and the eminent firm of platinum manufacturers to which he belongs have always shown. I stated to him the object which I had in view, and asked whether he would be willing to let me have the use of such residues from the working on

* From the *American Chemical Journal*, Vol. xx., No. 9.

the large scale of native platinum as might most probably yield davyum, any of the already known platinum metals separated therefrom to be returned. His reply was most cordial, and he obligingly offered the free use of such residues as I should designate. The feature in Kern's description of his new element which seemed to offer the best starting-point was the very slight solubility of the double chloride of davyum and sodium, and I suggested to Mr. Matthey that if, without too much trouble or disturbance of the usual course of working native platinum, the solution in *aqua regia* of the crude material, cleared by decantation from the insoluble osmiridium, &c., and by precipitation with ammonium chloride from the bulk of the platinum, could be evaporated to dryness with a large excess of common salt, and the residue re-dissolved in a minimum of water, any sparingly soluble material left behind by this second solution might be expected to contain the element sought for, and should be collected and sent to me. He very kindly promised that this should be done, but it was not feasible to take up the matter for some months. Meantime Mr. Matthey informed me that in the precipitation of platinum from certain liquors, a solution of ammonium chloride saturated with sodium chloride was often used, and that by evaporation of the clear solution (after precipitation) coloured crystals of impure sodium chloride with a little ammonium chloride were produced; this crude salt he thought might be worth examination, and he offered to send me some of it. In due time I received about a pound of this rose-coloured common salt, and later a specimen of the residue obtained by treating a lot of native platinum as I had suggested—35 kilogrms.* of Russian platinum mineral had yielded 13 grms. of residue, and of this about half was sent me. Mr. Matthey stated in a letter accompanying the sample of residue that the process had been unusually tedious, in consequence of the fact that in the second crystallisation, when the liquor was saturated with sodium chloride, such a dense mass of crystals formed to be re-dissolved only by the cautious use of cold water, as to require a very long time for solution and settlement. The two materials for examination, therefore, were this residue, obtained in accordance with my suggestion as to treatment of the complex solution of the metals from native platinum with sodium chloride, and the rose-coloured crystals of impure common salt from the regular course of procedure offered me by Mr. Matthey.

It was at once apparent on inspection of the former of these—the residue from special treatment—that it was not likely to be the sodio-chloride of any metal. It was an exceedingly fine grey powder, with minute glistening specks, and proved to be insoluble, not only in water, but in ordinary acids. It was hard enough to readily scratch glass, and even made some minute scratches upon rock crystal, when rubbed on by means of cork or wood. Seen under the microscope it exhibited a multitude of transparent colourless granules, with a smaller proportion of steel-grey or black, opaque and brilliantly lustrous little crystals, most of which were hexagonal plates with (plane) angles of 120° , and a few angles which measured a little more than 127° . Many fragmentary crystals were visible, and a few had the appearance of elongated blades. Many of the perfect crystals, while very minute, were beautifully sharp and well defined. Treatment with gently heated hydrofluoric acid drove off much silicon fluoride, and heating of what remained with concentrated sulphuric acid rendered soluble a small amount of zirconium sulphate with a trace of iron. The residue from the action of both acids was mixed with sodium chloride in fine powder, and at a dull red heat exposed to the action of moist chlorine gas; this, Wöhler's process for decomposing osmiridium, proved easily effective in consequence of the fine state of division of the material, and yielded

osmium volatilised mainly as the tetroxide, and iridium with a little rhodium left behind as sodio-chloride. It was evident that the material sent from London consisted merely of such part of the insoluble matter of the native platinum as *aqua regia* had left behind in so extremely fine a state of subdivision that it had remained suspended through the no doubt careful settling and decantation to which the platinum solution had been subjected. It is interesting to find so very dense a substance as osmiridium thus long held in suspension. After deduction of rather more than 1 per cent of hygroscopic moisture, the composition of this residue was approximately—

Quartz ..	40.8	
Zircon ..	15.4	
Osmiridium	43.8	= about
	100.0	
		{ Iridium 30.2 } (decomposition Rhodium 1.4 } by chlorine not Osmium 12.2 } quite complete).

(To be continued).

OBITUARY.

SIR EDWARD FRANKLAND.

It is with great regret that we announce the death of Sir Edward Frankland, which took place on Wednesday, the 9th inst., in Norway, where he had gone to indulge in his favourite pastime of salmon fishing. This country thus loses one of her most distinguished chemists, a man whose range was of extraordinary width and variety, whose brilliance as an experimentalist was unrivalled, and who made notable additions to our knowledge in almost every one of the numerous branches of chemical science to which he devoted his attention.

Born at Churchtown, near Lancaster, in 1825, he was educated at Lancaster Grammar School, and afterwards studied chemistry at the Museum of Practical Geology and in the laboratories of Liebig and Bunsen, at Giessen and Marburg. He had barely attained his majority when he began to engage in original work in pure chemistry, and even his earliest researches had an important influence on the development of chemical theory. Undertaken in conjunction with Kolbe and prosecuted in the laboratories of Playfair and Bunsen, these were at first analytical in character, their aim being the isolation and identification of the proximate radicals composing certain organic bodies. Soon, however, he began to turn his attention to synthetical problems, to the artificial building up of organic bodies, and here his efforts were rewarded by the important discovery of the organo-metallic compounds resulting from the direct union of a positive organic radical with a metal. It was in 1850 that he announced the preparation of compounds of zinc with methyl and ethyl, and predicted the existence of twenty other similar bodies. Intrinsically interesting as are these substances, their importance lies rather in the theoretical deductions which he drew from a consideration of their composition. In this way he evolved the conception that the atoms of zinc, tin, &c., had only room, so to speak, for the attachment of a fixed and definite number of the atoms of other elements; and this hypothesis, which was communicated to the Royal Society in 1852, was the basis of the doctrine of atomicity or equivalence of the elements which may be said to have dominated the course of all subsequent chemical theory since its enunciation. These views, together with others that followed from them, shared the usual fate of new ideas in failing to command universal and immediate acceptance; and that Frankland did not always receive full credit for them may be ascribed to the fact that, in the discussion of their value, their authorship was sometimes forgotten and other men came to be looked upon as their originators. This result was probably due in part to Frankland's standing aloof from

* This quantity, at the lowest proportion reported by Kern, viz., 0.0008 per cent, should have contained 0.280 grm. of metallic davyum, or, at the highest proportion reported, 0.045 per cent, 15.750 grms.

the controversies that arose, and to his general objection to self-advertisement, which it is permissible to say he sometimes carried so far as to shrink from legitimate self-assertion.

In applied chemistry, his first piece of work was begun in 1851, when he was appointed Professor of Chemistry in Owens College, Manchester, and related to the manufacture of water-gas. He also investigated the chemical composition of the gases evolved from different kinds of gas-coal, and incidentally invented a form of gas-burner which—like many other old inventions—has recently been brought forward as something new. By using two concentric chimneys, he made the waste heat of the flame raise the temperature both of the gas and the air consumed by the burner to 500 or 600° F., and so ensured a much more efficient light. But his most important contributions to applied chemistry had reference to water supply and sewage questions. When in 1865 he succeeded Hofmann as Professor of Chemistry at the Royal College of Chemistry (Royal School of Mines) he undertook to continue the monthly analysis of the water supplied to the metropolis, which Hofmann had begun a few months before for the Registrar-General. These monthly analyses, it may be mentioned, he continuously performed ever since that date, and his comments and reports form a most interesting and valuable feature of the Registrar-General's mortality returns in which they are to be found. This task involved the elaboration of a new method of water-analysis, since the processes then known he found seriously imperfect and untrustworthy, especially for the detection of pollution by sewage or animal matters, and it was only after two years of laborious experiments, in which he was helped by his then pupil, Professor H. E. Armstrong, that he succeeded in devising means with the accuracy of which he was satisfied. In 1868 he was appointed a member of the second Royal Commission on the Pollution of Rivers, and the Government provided him with a splendidly equipped laboratory in which to carry out the inquiries necessary for the purposes of that body. These researches occupied six years, and that they were on a most elaborate and exhaustive scale is sufficiently shown by the long list of subjects investigated. Among these were the chemical qualities of water from various geological strata and from different sources of supply, such as lakes, rivers, wells, &c.; the possibility of rendering water once polluted again wholesome; the propagation of disease by drinking water; the influence of hard water on health; the deterioration of water in mains and service pipes; and the quality of London water taken from the Thames. Of the last he did not at that time at all approve, because he held the belief that, no matter how satisfactory might be the chemical purification of polluted water by domestic or other artificial filtration, there was evidence that such water was still capable of propagating epidemic diseases. But this opinion was profoundly modified in the course of time as filtration became better understood and more effectively applied. Lecturing before the Royal Institution in 1896, he declared unequivocally in favour of the Thames as the source of water supply for London, and, after emphasising the astounding effect of sand filtration as practised by the London companies upon the living matter contained in raw river water, said that, with the provision of the storage reservoirs recommended by the Balfour Commission, London would possess an ample water supply, unsurpassed for palatability, wholesomeness, and general excellence. The purification of sewage and the means of preventing the pollution of rivers by trade refuse, &c., were among the other matters he investigated in connexion with the Commission.

Sir Edward Frankland was one of the few men who have spent a night on the very summit of Mont Blanc. This he did in August, 1859, in company with Tyndall, and the circumstance proved the starting-point for a long series of investigations in physical chemistry. On the summit the rate of combustion of stearin candles was observed,

with the object of discovering whether the rate of burning of bodies needing a supporter of combustion is independent of the density of the atmosphere in which they are burnt—a question which was answered in the affirmative. But Frankland noticed that the candles gave a very feeble light, and this observation induced him on his return to England to institute a series of experiments on the source of light in luminous flames. The results led him to believe that the light was not always due to solid particles, since many luminous flames had none, and he showed that incandescent gases and vapours emit light in proportion to their density—hydrogen, for example, having a luminous flame, if burnt in a pressure of 10 or 20 atmospheres. Other experiments, in which Sir Norman Lockyer also had a share, he regarded as showing that brilliancy of light and continuity of spectrum are not peculiar to ignited solid or liquid matter, but that the same phenomenon is produced by the ignition of compressed gases. A consequence of this discovery was the conviction that the sun cannot be ignited solid or liquid matter, but that, at least, the photosphere, or outer layer of luminous matter, must consist of gases or vapours only.

In physiological chemistry he took part in a crucial experiment to settle the vexed question of the origin of muscular power. He, Fick, and Wislicenus, proposed to confine themselves to a non-nitrogenous diet and ascend the Faulhorn, taking a strict account of the greatest possible muscular oxidation by determining the amount of nitrogen expelled from each body before, during, and after the ascent. In the end, however, he was unable to make the experiment on his own person, but Fick and Wislicenus performed the ascent while he did the difficult laboratory experiments and calculations necessary for the interpretation of the results. The latter, in his opinion, left little room for doubt. He thought it impossible to account for more than a small fraction of the work done in the ascent by the force evoked by the transformation of muscle into the quantities of its products observed by the experimenters, and he concluded that a large proportion at least of the force was developed by the oxidation of non-nitrogenous substances, such as fat.

A few personal details of his life may be added. He held professorships of chemistry successively in Owens College, St. Bartholomew's Hospital, the Royal Institution, where he followed Faraday, and the Royal College of Science, South Kensington, retiring from the last in 1885. The Royal Society, which made him a Fellow in 1853, gave him a Royal medal in 1857, and he also acted as its foreign secretary. Abroad, the French Academy of Sciences recognised his merits by making him a corresponding member in 1866, and he was also a foreign member of the Academies of Sciences of Bavaria, Berlin, St. Petersburg, Upsala, America, and Bohemia. Oxford gave him the degree of D.C.L. in 1873, and Edinburgh that of LL.D. in 1884. He was the first president, in 1877, of the Society of Chemical Industry, and served as president of the Chemical Society in 1871, being one of the six ex-presidents entertained at the recent banquet. The honour of K.C.B. was bestowed on him in 1897.

He was twice married, first to Sophie, daughter of Herr F. W. Fick, of Hesse-Cassel, who died in 1874, and second in 1875 to Ellen Frances, daughter of Mr. C. K. Grenside, of Wimbledon. She also predeceased him. Professor Percy Frankland, of Birmingham, is the second son of the first marriage.—*The Times*.

PROFESSOR ATTFIELD contributes the following to a contemporary:—

“The Editor asks me for personal reminiscences of my old chief Frankland, whose death all science is deploring. For five years, 1857 to 1862, I was, as Demonstrator, daily with him as Lecturer in Chemistry at St. Bartholomew's Hospital Medical School, and I was his lecture-assistant and one of his research-assistants either at the Hospital, the Royal Institution, or the Military College,

Addiscombe; so that during the period mentioned I saw a great deal of him. My first quarter of an hour with him—at Owens College, Manchester, at the time of the Art Treasures Exhibition, 1857, and within a week of his appointment to Bartholomew's, where I had already been under Stenhouse for three years—revealed his great powers of perception and his transparent simplicity and nobility of character. Within twenty minutes he had found enough in me for reliance, I enough in him to make me long to work under him. Yearly my respect for him deepened. To his students he was ever approachable, patient, and informing; to his colleagues ever genial, loyal, and chemically and physically helpful. The world knows of his ability as a chemist and physicist; but he was a skilled mechanic also, an admirable worker in metal, wood, and glass. In his prosecution of research and the publication of his discoveries his one aim seemed to be the revelation of truth, never the glorification of self. The why and the wherefore, the whence and the whither, seemed always to beckon him, and if ever he turned aside at the earnest request of clients it was only a case of *reculer pour mieux sauter*. 'We must live,' he used to say, with something between a smile and a sigh. To his helpers he was kind, yet firm—the kinder because firm—in his demands for accuracy. While assisting him in experimentally ascertaining the effect of diminished atmospheric pressure on combustion, it needed effort to get from him his personal experience in ascending Mont Blanc and spending a night on its summit; but what he told me implanted in me that form of joy in the beautiful which mountains, little and big, chiefly the former, afterwards afforded me for five and twenty years, and which is not excelled by any of the joys of earth. He turned over to me the conduct of the Hospital school class in practical chemistry, and encouraged me to print the results of my educational experience. Against his own interest, as he said, he exerted himself to secure my election to a professorship at the Pharmaceutical Society in 1862, and when, a year afterwards, I confided to him my disappointment that a certain Committee had refused me an induction coil with which to carry on my researches on the spectra of electrically ignited gases in semi-vacuous tubes, he reminded me, in spite of his love for pure science, that I had been chosen instead of three men of greater experience in research because of my greater knowledge of the applications of chemistry to pharmacy, and that I must order my life accordingly. Through him I had become known to men like Faraday and Tyndall, Geissler and Casella, Kolbe and Strecker, Gassiot and Playfair, men who gave me help through their respect for Frankland. His advice, and letters of introduction to two Universities, much aided me in obtaining a degree. It was he who invited me to become a candidate for the Fellowship of the Royal Society. Small wonder that I loved him. The powerful searchlight of his brain could all but reveal the atoms of matter, could illumine the photosphere of the sun, could penetrate corners in vitality; Nature's forces yielded up their secrets under its influence, welcoming it as a sister to themselves. Yet he was unselfish and sympathetic, not kinder to me than to all by whom he was immediately surrounded. Alas! he has gone.

"JOHN ATTFIELD.

"Watford, August 15, 1899."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 3. July 17, 1899

Combination of Carbon Disulphide with Hydrogen and Nitrogen. — M. Berthelot. — When a mixture of

hydrogen and carbon disulphide is submitted for some time to silent electric discharge, the hydrogen is absorbed and a compound appears to be formed having the formula $C_2H_2S_4$. This may represent either oxalic acid in which the oxygen is replaced by sulphur, or a persulphide derived from glycollic aldehyde. The same set of experiments were tried with nitrogen instead of hydrogen. In the two experiments the proportion of nitrogen and carbon disulphide was $4CS_2 : N_2$ and $7CS_2$ to N_2 .

Compounds of Nitrogen with Oxygen.—M. Berthelot.—During the process of purifying argon from nitrogen, the author measured the proportion between the nitrogen and oxygen as the mixture is subjected to the electric discharge. The results are interesting, as showing the successive and gradual formation of the different oxides of nitrogen. It appears that gaseous nitrous acid is always formed first, even in the presence of an excess of oxygen, and that it only changes into peroxide of nitrogen very slowly. The dioxide of nitrogen formed under the action of the electric spark on the mixture of nitrogen and oxygen combines, first with one atom of oxygen, forming nitrous anhydride, $2NO + O = N_2O_3$; then it unites with a second atom of oxygen, forming peroxide of nitrogen, $N_2O_3 + O = 2NO_2$.

Chromic Acetate.—A. Recoura.—The author describes the isomeric forms of chromic acetate. These compounds are particularly interesting:—(1) Because chromic acetate shows four isomeric forms, the other salts but two; (2) because whilst in the preceding salts the form stable in solution is the normal salt, in the case of the acetates the stable forms are those which are not true salts. The formula $Cr(C_2H_3O_2)_3$ is taken for chromic acetate. The preparation and properties of the various forms are described.

Journal de Pharmacie et de Chimie, Series 6, Vol. ix., No. 4.

A New Method for the Estimation of Carbonic Oxide. — MM. Schlagdenhauffen and Pagel. — Inserted in full.

The Alteration of an Iodoformed Lint.—P. Rouvet. —The author has observed that iodoformed lint undergoes an alteration after keeping. On opening a packet an odour of putrefying organic matter was observed; the oiled parchment paper in which it was wrapped had a dark brown tint and was specked with small brilliant white crystals. By micro-chemical and ordinary reactions these crystals were found to consist of iodide of zinc, showing that the iodoform had been reduced, as they were the result of the iodoform vapour, or hydriodic acid, on the galvanised iron case in which the lint had been packed. The oiled parchment paper was also connected with the alteration, and the author recommends that paraffined paper should be substituted in future.

No. 5.

The Detection and Estimation of Bromoform in Toxicology.—A. Richaud.—In detecting bromoform in the presence of organic matter by entanglement with a current of steam, we are able to collect, almost integrally, all the bromoform in a quantity of water not exceeding 75 to 100 c.c. It then suffices to add a few morsels of potash, to fit the flask with a vertical refrigerator, and heat gently for an hour or an hour and a half to completely transform the bromoform into bromide.

No. 6.

On the Nitrated Gaïacols.—H. Cousin.—Two nitrated gaïacols are known—the 4-nitrogaïacol prepared by H. Rupe by the action of nitric acid on 4-nitroso-gaïacol, and a dinitrated gaïacol (4:6-dinitro-gaïacol) obtained by Hertzog by the action of a current of nitrous vapours on an ethereal solution of gaïacol. The author has employed two new methods for preparing these de-

r.vatives:—5 c.c. of crystallised gallicol are dissolved in 50 c.c. of chloroform, then gradually add—while keeping the liquid cool—a mixture of 5 c.c. of fuming nitric acid and 20 c.c. of glacial acetic acid; to the dark brown liquid 200 c.c. of water are added, and the chloroformic layer collected. On evaporation, a reddish brown crystalline mass is left, which is purified by several crystallisations in alcohol at 50°; this is identical with the body found by Hertzog. The mononitrated gallicol was prepared by dissolving 10 c.c. of acetyl-gallicol, or of acetic ether of gallicol, in 10 c.c. of glacial acetic acid, and gradually adding a mixture of 10 c.c. of fuming nitric acid and 10 c.c. of acetic acid; a lively reaction takes place, nitrous vapours being given off. After cooling, water precipitates a solid material, which is drained by the filter-pump and purified by crystallisation in alcohol at 90°. In this manner a mononitrated acetyl-gallicol is obtained in the form of fine, nearly white needles, insoluble in water, soluble in boiling alcohol, fusing at 100–101°.

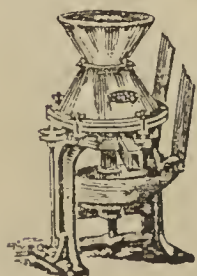
The Action of Amylic Alcohol of Fermentation on its Soda Derivative.—M. Guerbet.—One kilogram. of amylic alcohol and 130 grms. of sodium are placed in a flask fitted with a vertical condenser and heated gradually until boiling; this is kept up for twenty-four hours, and the mass taken up with water; add sulphuric acid, but leaving the solution still slightly alkaline, remove the supernatant oily layer, wash it with water, and dry over carbonate of potassium. After several rectifications, 125 grms. of a neutral liquid, boiling at 210–211°, can be separated. There remains in the flask a small quantity of an oily compound from which 10 grms. of a neutral liquid can be separated, boiling at 173–175° under 8 c.m. pressure. To the alkaline solution left, add an excess of sulphuric acid, when a mixture of acids is formed, which is dried over sulphate of soda; of these, isovaleric acid is the principal. These three compounds—the alcohol ($C_{10}H_{22}O$), the acid ($C_{10}H_{20}O_2$), and isovaleric acid—result, no doubt, from the action of amylic alcohol on its soda derivative; one molecule of each of these compounds will react on the other according to the equation $C_5H_{11}NaO + C_5H_{12}O = C_{10}H_{22}O + NaOH$, and the soda thus formed oxidises the amylic alcohol by the reaction $C_5H_{12}O + NaOH = C_5H_9NaO_2 + 4H$.

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THE CHEMICAL NEWS.

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SOME DRAWBACKS TO THE USE OF ACETYLENE.

By Prof. J. VÉRTÉSS.

WHILE coal-gas has had to struggle for a whole century before becoming the almost universal lighting agent, its rival, acetylene, has already—after only a short time—achieved a certain success. Of course acetylene is not a newly discovered body, but it is only since the economic production of carbide of calcium that it has become practicable as a lighting agent.

Theoretically the production of acetylene is a very simple matter, but such is not the case practically.

Carbide of calcium, as is well known, is a black, crystalline, very hard material, not decomposed by heat, but easily decomposed by water into acetylene and lime. It has a density of 2.2, and it is not soluble either in petroleum or in benzene.

Concentrated acids have no action on it.

Acetylene consists of a colourless gas, with a penetrating odour of garlic. Its density is 0.1; 1 litre of acetylene weighs 1.16 grms. It is easily soluble in water, and can be liquefied at 0° under a pressure of 48 atmospheres. In this state it is very explosive. It burns with a white flame, without a dark cone; the temperature of this flame is lower than that of coal-gas.

Unfortunately, lighting by acetylene still presents numerous difficulties, to which I am desirous of calling the attention of specialists and others, now that I have had the opportunity of examining the installation which supplies the town of Veszprim in Hungary.

Let us first consider the carbide, the source of all the trouble. This body is never pure, but always contains at least 20 per cent of impurities. Theoretically, 64 parts by weight of carbide should give 26 parts by weight of acetylene,—that is to say, that 1000 grms. of carbide ought to produce 406.25 grms. of acetylene, and, as 1 litre of this gas weighs 1.16 grms., we ought to get 350 litres. But the continental factories will not guarantee a return of more than 300 litres, and practical experience shows that we can hardly depend on more than 280 to 290 litres. It is true that the estimation of the return is not free from causes of error, inasmuch as during the weighing the carbide absorbs a certain amount of moisture from the atmosphere; this causes a loss of acetylene. But the small errors which result, when calculated on 1000 grms. of material, are multiplied in proportion. We are obliged to work with small quantities, seeing that only 100 grms. of material give off 30 litres of gas, and it is difficult to arrange graduated gas-holders to store such large quantities. Further, the carbide is so little homogeneous that several samples must be tested and examined in order to obtain a mean value. If, on the other hand, we only take 10 grms., the error resulting from the disengagement of acetylene in the air will be multiplied one hundred times if the results are calculated, as they should be, on 1000 grms. I have examined the manner in which the carbide behaves in the presence of acids, and I found that concentrated sulphuric acid has no action on this body; but no matter how little water the acid may contain, bubbles of gas are formed until the whole of the water is consumed. This property of the carbide of not being attacked by concentrated sulphuric acid enables us to estimate its producing power of acetylene. I have made several experiments in this direction, and the results obtained were fairly correct and concordant.

I must here again mention that the carbide contains

sulphur, phosphorus, and nitrogen, from which it results that the acetylene will be contaminated with sulphuretted hydrogen, phosphoretted hydrogen, and ammonia. The acetylene must therefore be purified to the same extent as is coal-gas, for fear that its use in closed places might cause serious accidents.

But the greatest drawback of all is that acetylene burns with a smoky flame. Certainly the flame does not smoke at first, but after 200 or 300 hours smoke begins to be formed. This is caused by the burners attaining a temperature higher than that of the decomposition of acetylene, and thus the gas is decomposed into carbon and hydrogen.

I have also noticed a very curious phenomenon in the gas-pipes; I there found a deposit of finely-divided carbon like soot. I also found a very remarkable liquid condensation, consisting of carbides of hydrogen. These bodies are also formed in the generators, whence the necessity of using syphons. We thus see that it is quite erroneous to imagine that acetylene does not require purifying.

There is still another inconvenience resulting from impurities contained in acetylene. It is by no means uncommon to see, in a closed place, a sort of fog fill the room after a longer or shorter interval. What is the cause of this phenomenon? The acetylene is decomposed in the burner, the carbon is deposited while the hydrogen burns, giving rise to the formation of watery vapour; and it is this, in conjunction with the ammonia, the sulphuretted hydrogen, and the phosphoretted hydrogen, which produces the fog, causing headache and nausea.—*Chem. Zeitung*, 1898, p. 174.

THE ANALYSIS OF ACETYLENE.

By WALTHER HEMPEL and LEOPOLD KAHL.

AMONG the impurities which accompany acetylene, the most important—after the oxygen and nitrogen of the air—is phosphoretted hydrogen. As calcium carbide leaves on decomposition a residue formed principally of calcic hydrate, carbide and silicide of iron, and carborundum—that is to say, a residue with a strongly alkaline reaction—it is certain that acetylene does not contain any sulphur in the form of sulphuretted hydrogen. It is true that some writers have noticed the presence of a small quantity of sulphur, but it is probable that it existed in the state of sulphurised organic compounds. A sample of calcium carbide from New York which we analysed contained from 6 to 8 per cent of carborundum and silicide of iron, and 0.2 to 0.24 per cent of silica.

As the presence of hardly noticeable quantities of phosphoretted hydrogen may make the acetylene spontaneously inflammable, it is of the greatest importance to entirely eliminate this body. This could be done by using only a carbide free from phosphorus, or by purifying the acetylene by means of suitable reagents. In any case it is necessary to have methods of gas analysis enabling us to estimate rapidly and exactly the quantity of phosphoretted hydrogen present in the acetylene.

Lunge (*Zeit. Anorg. Chem.*, 1897, p. 651) has recently proposed decomposing, by means of water, known quantities of carbide and passing the acetylene produced through sodic hypochlorite. The phosphoretted hydrogen is thus oxidised to the state of phosphoric acid, which is easy to estimate by ordinary gravimetric means. It is certain that this method gives very exact results, but unfortunately it requires too long a time. In our opinion it is essential to have a method permitting the volumetric separation of the acetylene from the phosphoretted hydrogen, so that the analysis can be finished in a few minutes.

Such is the problem we proposed to solve, and with this view we have tried a large number of solutions which might lead us to the desired end. We prepared a fairly large quantity of phosphoretted hydrogen by heating an

alcoholic solution of potash lye with white phosphorus, the gas produced being collected in a glass gas-holder. As this phosphoretted hydrogen contains a fairly large proportion of hydrogen and a little air, the figures given below will not be found to be of scientific accuracy. The acetylene was freshly prepared for each series of experiments.

To put the gas in contact with the reagents we operated in the following manner:—Into a pipette filled with mercury we introduced 1 c.c. of the reagent and then 100 c.c. of gas; after having shaken vigorously for three minutes, we measured in a gas burette the fraction unabsorbed.

The figures in the following table show the quantity of gas absorbed by 1 c.c. of the reagent.

Reagent used.	Phosphoretted hydrogen absorbed. C.c.	Acetylene absorbed. C.c.
I. 1 c.c. of cuprous chloride in hydrochloric solution prepared by C. Winkler's method	39.8	9.4
II. 1 c.c. of cupric chloride in hydrochloric solution, obtained by dissolving 10 grms. of crystallised cupric chloride, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, in 100 c.c. of water and 5 c.c. of concentrated hydrochloric acid	8.6	5.2
III. 1 c.c. of cupric sulphate in sulphuric solution, prepared by dissolving 15.6 grms. of crystallised cupric sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, in 100 c.c. of water and 5 c.c. of sulphuric acid at 25 per cent by volume	8.8	0.2
IV. 1 c.c. of sodic hypochlorite, prepared by dissolving 10 grms. of crystallised carbonate of soda in 100 c.c. of water, adding an excess of chloride of lime, and filtering	3	0.6
V. 1 c.c. of sodic hypobromite, prepared by dissolving 100 grms. of caustic soda in 1250 c.c. of water and adding 25 grms. of bromine	Explosion.	
VI. The preceding solution diluted with four volumes of water	—	1.3
VII. Sodic hypochlorite, prepared by passing chlorine gas through soda-lye. This reagent was brought, by the addition of caustic soda and water, to the same alkalimetric titration and the same value in active chlorine as Solution V.	—	0.7
VIII. Permanganate of potash at 5 per cent.	3.2	2.6
Permanganate of potash at 1.25 per cent	1	1.2
IX. Nitrate of silver at 3 per cent	—	1.6
X. Cupric sulphate in nitric solution, obtained by dissolving 78 grms. of sulphate of copper, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, in 250 c.c. of water and 250 c.c. of concentrated nitric acid.	1.2	0.8

As can be easily seen, the sulphate of copper in sulphuric solution is the best reagent for separating phosphoretted hydrogen from acetylene.

A large number of trials made with the view of effecting the absorption in gas pipettes has shown us that light has a great influence on the results obtained. We have attempted to prepare in a double gas pipette filled with acetylene a solution of cupric sulphate saturated with acetylene; but when left to itself the cupric solution continued to absorb fresh quantities of acetylene, even in diffused light. The same phenomenon occurred with sodic hypochlorite.

Following up our researches, we eventually found that acetylene behaves differently, according to whether it is put in contact with cupric sulphate only or with cupric sulphate and metallic mercury in the presence of phosphoretted hydrogen. We found that, in the presence of mercury and an excess of cupric sulphate, the diminution of volume due to absorption is exactly four times greater than the volume of the phosphoretted hydrogen present.

It was therefore important to know if acetylene free from phosphoretted hydrogen would behave in the same manner, and we found that in both cases the result was the same—2 c.c. of cupric sulphate in acid solution absorbed 0.4 c.c. of gas.

We give below the results obtained with a mixture of acetylene and phosphoretted hydrogen at 52.4 per cent. The gaseous mixture was well shaken up with 3 c.c. of a sulphuric solution of cupric sulphate saturated with acetylene. The small differences are partly due to the difficulty experienced in always saturating the reagent with the same quantity of acetylene.

Acetylene used.	Phosphoretted hydrogen at 52.4 per cent used.	Diminution in volume found.	Actual phosphoretted hydrogen.	Phosphoretted hydrogen found by absorption, admitting that the phosphoretted hydrogen equals a quarter of the diminution of volume.
92.8	5.6	11.2	2.9	2.8
90.2	7.4	13.4	3.9	3.4
94.6	2.4	4.6	1.2	1.15
92.2	5.2	10.6	2.7	2.65
94.0	3.2	8.3	1.67	2.0
82.0	5.4	11.0	2.82	2.75

To sum up, for determining the quantity of phosphoretted hydrogen contained in acetylene, the gas is measured in a gas burette filled with mercury, and from thence transferred to another burette filled with mercury and 3 c.c. of cupric reagent saturated with acetylene. After shaking for three minutes, the volume of the unabsorbed gas is measured; a quarter of this volume represents the phosphoretted hydrogen present.—*Zeit. f. Angew. Chem.*, 1898, No. 3, p. 53.

THE ESTIMATION OF OXYGEN IN COPPER.

By MAURICE LUCAS.

IN this paper I have only dealt with the estimation of suboxide of copper in commercial copper.

Such copper now-a-days generally contains only very slight traces of foreign matters, but it always contains a notable quantity of oxygen, on which different observers are far from being in accord; and if analysis is admitted to be a gauge of the quality of a copper, the estimation of this oxygen is very necessary.

It is combined to a great extent with the copper in the state of suboxide of copper, Cu_2O ; the proportion of oxygen combined with metals other than copper, and with the metalloids, is negligible, except sometimes in the case of arsenic, which is generally admitted to be in the state of arseniate of copper or of lead.

It is impossible to have a complete check of the esti-

mation of suboxide of copper, because we cannot effect the synthesis of the melted mixture, copper—suboxide of copper.

It is for this reason that I have compared the results obtained;—1st, by heating in hydrogen and measuring the loss of weight; 2nd, by attacking with nitrate of silver and estimating the insoluble residue.

I have varied one by one the conditions under which this latter method was carried out, and have finally decided on a series of operations which satisfies the following conditions:—

- Constant results with the same sample.
- No variations with the sample taken.
- Close agreement with the reduction by hydrogen.
- No result with copper electrolysed by M. Riche's method.
- By attacking the suboxide only, the quantity of copper contained in the residue is well in *rappor*t with M. Hampe's formula.
- The simultaneous attack of the copper and of the suboxide gives the same results as if the attacks were conducted separately.
- If a strip of copper is placed in neutral nitrate of copper, it does not on filtration leave any precipitate containing copper.

Samples used.—The experiments were carried out on a test sample of copper to which 3 per cent of suboxide of copper had been added while melted (2.75 per cent remained), and on a sample of calumet copper. These two samples did not contain sulphur or arsenic, and only 0.001 per cent of lead and iron.

I. Reduction by Hydrogen.

This method of estimation did not appear to me to be a trustworthy check, for, in order to make certain that the reduction is complete, it is necessary to test for any suboxide remaining—that is to say, to admit *à priori* an error in the method of analysis. Nevertheless, it has been done by closely following Hampe's instructions (*Zeit. Anal. Chem.*, vol. xiii., p. 188; Fresenius, "Anal. Quant.," p. 1018), and gave the following results:—

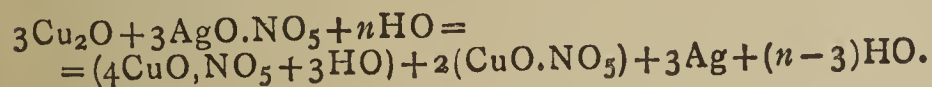
Test copper	2.75
Calumet copper	0.68

and, by fusing the latter in hydrogen, 0.75.

The coppers thus reduced to a constant weight were assayed by Hampe's method modified; they did not then contain any suboxide.

II. Attack by Nitrate of Silver.

Hampe's Method.—Hampe showed that by the action of nitrate of silver the copper was dissolved, and the suboxide transformed into basic nitrate of copper according to the formula:—



This basic nitrate is the same as that obtained by Gerhardt by boiling the neutral nitrate with the oxide CuO or an alkali.

The copper in the insoluble residue is estimated, and by following Hampe's method very closely we obtained—

Test copper	2.88.
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Hampe's Method modified.—The solution of nitrate of silver is prepared by attacking silver with nitric acid and continuing the crystallisations until the mother-liquors are no longer acid; the crystals are dried over quicklime and protected from the light; a 5 per cent solution was prepared from these crystals, allowed to stand for a time, then decanted into a red glass flask.

Strips of copper of about 0.15 m.m. thickness, carefully rolled, and cleaned with glass paper, are attacked, using about 1 grm. of copper to 120 c.c. of the solution, for fifteen hours *in vacuo*, without shaking. The residue is filtered on a plug of asbestos and washed with cold

water until no more copper passes through. The residue is again attacked for two hours *in vacuo*, and a test made to find if any more copper has been dissolved; this residue is now filtered, washed, and attacked with nitric acid. The silver is separated by hydrochloric acid, and the copper estimated by electrolysis and its weight multiplied by 1.689; it must be tested to make sure that it contains no silver.

The following results were obtained by this method:—

	Weight of sample.	Suboxide of Cu per cent.
Test copper ..	10 grms. 1 grm.	2.75, 2.78 2.70, 2.76, 2.71, 2.74, 2.65, 2.79
Calumet copper	10 grms. 1 grm.	0.63, 0.65 0.68, 0.68, 0.68.

The copper was also estimated colorimetrically, by means of ferrocyanide of potassium, a method which is found to be the most convenient for the small proportions which are generally present. In a future paper I shall point out the necessary precautions to take. By this method I have obtained the following results:—

	Cu ₂ O per cent.	
	Rolled strips.	Turnings.
Calumet copper	0.68, 0.69	0.69
Société des Metaux:—		
Electrolytic copper from Bornel	0.49, 0.49	0.52
Civet copper marked N.A.	0.40, 0.48	0.52
Société de Biache St-Waast:—		
Electro copper	0.76, 0.77, 0.78	0.78
Arizona copper	0.34, 0.34, 0.34	0.34
Boléo copper	0.80, 0.70, 0.76, 0.72	0.78

III. Conditions for Working.

The following assays were made with two samples, but only making one variation at a time from the method adopted above; they serve to justify the precautions recommended.

Sample taken.—I have noticed that, by diminishing the amount of the sample used, the results given by Hampe's method were progressively increased; I thus obtained as much as 6 per cent on the test copper.

The modified method did not show such irregularities.

Solution of Nitrate of Silver.—Nitrate of silver is reduced by light and becomes acid; we cannot correct its acidity by adding silver; the addition of caustic soda introduces carbonates, the inconvenience of which we shall see later on.

The assays made with 50 per cent nitrate of silver solution gave results both low and irregular; the silver was in compact morsels. The action is too rapid, and is impossible to regulate.

Treatment of Turnings.—The treatment of turnings generally gives results identical with those from rolled strips, but we can never be quite certain that no oxide is present on the surface. It is for this reason that I prefer to use rolled strips.

Copper melted in an atmosphere of hydrogen, and rolled thin, is completely dissolved by nitrate of silver, which shows that rolling, when carefully done, does not imprison any oxide in the metal.

Attack in the presence of Air.—These results are always higher (3.15 instead of 2.75). Now:—

1st. By exposing a neutral aqueous solution of nitrate of copper to the air, filtering on asbestos, and washing with cold water, the asbestos does not take any colour on adding ferrocyanide of potassium.

2nd. The same is the case with a mixture of neutral nitrate of copper and nitrate of silver.

3rd. But if 3 grms. of precipitated silver are added to the neutral nitrate of copper, and the liquid filtered, after twenty-four hours' contact with the air, 0.003 grm. of copper is found on the asbestos; this is precisely the

difference between the quantities of copper weighed to obtain 3.15 and 2.75 per cent. of suboxide of copper in 1 grm. of test copper.

Attack in the presence of Carbonic Acid.—In a current of carbonic acid, or even simply in an atmosphere of carbonic acid, we obtain too low results (0.7 instead of 2.75); copper is dissolved.

A current of carbonic acid through water holding in suspension the hydrate, carbonate, or the basic nitrate of copper, dissolves as much as 0.034 grm. of copper per litre, which is re-precipitated on boiling or by exhaustion under the air-pump. Caustic soda, which generally contains carbonates, must not be used for correcting the acidity of nitrate of silver.

Attack in the presence of Hydrogen.—With a current of hydrogen, or simply in an atmosphere of hydrogen, the results obtained are too low (1.8 instead of 2.75).

Attack in the presence of Nitrogen.—With a current of nitrogen in a liquid freed from air, we obtain good result: this process *in vacuo* has the advantage of making the action more rapid by agitation.

Filtration.—Filtration through paper gives higher results than filtration through asbestos. If we filter the neutral nitrate of copper successively through several filter-papers, it is noticed that in spite of the most prolonged washings, which eventually do not carry off any copper, all the filter-papers are still coloured red by ferrocyanide of potassium: this does not occur when using either asbestos or glass-wool.

The quantity of copper, which is variable, does not exceed 2 m.grms. for 10 c.m. of filter-paper.

Washings.—These washings, which do not present any difficulty, take a very long time when we operate on 10 grms.; it is for this reason that I have adopted 1 grm. as sufficient to work on.

Solution of the Basic Nitrate of Copper.—Independently of the process I have just described, we can effect the solution of the basic nitrate of copper by warm dilute sulphuric and hydrochloric acids, or by ammonia. Hydrochloric acid at 5 per cent dissolves both more copper and less silver; it should be used in two successive portions. —*Bull. Soc. Chim.*, Series 3, vol. xix.-xx, No. 16-17.

SEPARATION OF PROTEID BODIES FROM THE FLESH BASES BY MEANS OF CHLORINE AND BROMINE.

By H. W. WILEY.

In dry, finely-ground animal matters, from which the fats have been thoroughly extracted with ether, it is possible to effect an easy separation of the nitrogenous bodies into three groups. These groups, for purposes of dietetic study, are sufficiently distinct to afford a safe basis of valuation of the different nitrogenous constituents. The process which has been adopted in the laboratory of the Division of Chemistry, Department of Agriculture, for this separation is given in detail here.

Details of Method.

In the dry, fat-free, finely-ground animal substance the nitrogenous bodies soluble in water may be separated by first thoroughly exhausting the material with cold or lukewarm water, and afterwards with water near the boiling temperature. By this method the water-soluble constituents of the nitrogenous substances are thoroughly removed. Having determined the total percentage of nitrogen in the whole sample, the residual insoluble nitrogen is determined in the residue left after extraction. This percentage multiplied by 6.25 gives the total quantity of insoluble proteid matter contained in the animal material. In the filtrate the soluble proteid matter which has been dissolved by the water may be completely

thrown out of solution by treatment with bromine in the manner about to be described.

About 1-grm. portions of the dry animal material are washed with ether by decantation, using from 50 to 100 c.c. of ether for each sample, and decanting the ether through filters which are afterwards used to receive the portion of the sample insoluble in hot water. After allowing the ether to evaporate, the samples are treated first with cold and then with hot water, this washing also being by decantation, the total amount of water used being from 300 to 400 c.c. The undissolved residues are brought on to the filter with the last portions of water. The nitrogen in the residues on the filters is determined by the Gunning method.

The filtrate from the insoluble portions of the meat is received in Kjeldahl flasks and used for the separation of the soluble proteid nitrogen by bromine. The filtrate is first acidulated with two or three drops of strong hydrochloric acid, and then about 2 c.c. of liquid bromine are added and the contents of the flask vigorously shaken. If the bromine be all taken up more is added until finally a globule of $\frac{1}{2}$ c.c. of liquid bromine is left undissolved and the supernatant liquid is thoroughly saturated with bromine. The mixture is then allowed to stand overnight, by which time the precipitate will have settled. The supernatant liquor is passed through the filter and the precipitate in the flask washed by decantation with water, the globule of undissolved bromine serving to saturate the wash water so that it is unnecessary to use additional bromine water for the washing. The filter containing the precipitate is returned to the same flask in which the precipitation has taken place, and the nitrogen therein determined by the Gunning method. The sum of the nitrogen in the part insoluble in water and the part precipitated by bromine is subtracted from the total nitrogen determined on the original sample, and the difference gives the total nitrogen in the flesh bases.

Factors for Calculation of Total Nitrogen.

The factors used for calculating the total nitrogenous bodies are as follows:—

For the part insoluble in water, $N \times 6.25$

For the part soluble in water and precipitated by bromine, $N \times 6.25$.

For the flesh bases, $N \times 3.12$.

This method is based upon investigations reported by Rideal and Stewart (*The Analyst*, 1897, xxii., 228 *et seq.*) last year.

These writers recall some of the experiments made in 1876, in which it was shown that a current of chlorine gas, conducted through an aqueous solution of proteid matters, produces a precipitate which is of a quite constant composition, and one which can be collected, dried *in vacuo*, and weighed. They describe particularly the use of this reagent in precipitating gelatin prepared from the high-grade commercial article. They show that the total quantity of gelatin can be accounted for from the weight of the precipitate by multiplying the weight of the precipitate obtained by the factor 0.78. The authors also point out the possibility of using bromine for chlorine for the precipitation, and state that the studies of the use of bromine are under way. They call attention to the fact that as early as 1840 chlorine had been used by Mulder for the precipitation of soluble proteids, and refer to a paper of his published in Berzelius's *Jahresbericht*, vol. xix., p. 734, in which he states results on precipitation quite similar to those secured by Rideal and Stewart.

At the close of their paper Rideal and Stewart mention the work in this direction of De Vrij (*Ann. Pharm.*, lxi., 248), Thénard (*Mém. d'Arcueil*, ii., 38), Mulder (*Bulletin en Néerlande*, 1839, 153), and Berzelius (*Jahresbericht*, xix., 729), on the same subject.

Allen and Searle (*The Analyst*, 1897, xxii., 258—263), acting on the suggestion of Rideal and Stewart, worked out the bromine method by applying it to various soluble proteids, including the whole range from albumen to

peptone. In the application of this test to commercial gelatin the following process was employed:—

Fifty grms. of commercial gelatin were dissolved in warm water and the solution diluted to half a litre. In 10 c.c. of this solution, corresponding to 1 gm. of the gelatin, the nitrogen is determined directly by the Gunning-Kjeldahl process. Another portion of 10 c.c. is treated with an excess of bromine in the following manner:—

The solution is first brought to a volume of 100 c.c. with water, and placed in a conical beaker with a sufficient quantity of hydrochloric acid to produce distinct acid reaction. A saturated solution of bromine water is added in considerable excess, and the liquid stirred vigorously for some time. The precipitate which separates is flocculent when first formed, but becomes more viscous after stirring, and adheres for the most part to the sides of the beaker, which, with its contents, is allowed to stand for about half an hour, or until all the precipitate is settled. The supernatant liquor is decanted through an asbestos filter. The precipitate adhering to the beaker is washed several times with cold distilled water, and the washings poured through the filter. Occasionally, when most of the free bromine is washed out of the precipitate, the liquid does not filter clear. It is therefore advisable to keep the washings separated from the filtrate, and, if necessary, wash with sodium-sulphate solution or with bromine water. The nitrogen in the precipitate is determined by the Gunning-Kjeldahl process as follows:—

The precipitate which has been collected on the asbestos filter, together with the asbestos, is returned to the beaker in which the precipitation took place; 20 c.c. of strong sulphuric acid are added, the beaker covered with a watch-glass and placed on a wire gauze over a lamp. When frothing has ceased, about 10 grms. of powdered potassium sulphate are added and the liquid boiled until colourless. After cooling, it is distilled with water, and the ammonia distilled off and determined in the usual way. The percentage of nitrogen found, when multiplied by the factor 6.33, or in the case of gelatin by 5.5, gives the amount of proteid matter precipitated by bromine. In the commercial gelatin above mentioned the nitrogen content was found to be 14.1 and 14 per cent, respectively, on two determinations. Solutions of creatinin, asparagin, and aspartic acid were found to yield no precipitates with bromine, but bromine was found to precipitate all albumen, acid albumen, and all peptones formed by the digestion of albumen with pepsin.

Application to Commercial Meat Extracts.

On applying the bromine method to commercial meat extracts the following results were obtained. The solutions of the Bovril preparations were not previously filtered, and therefore the figures contain the nitrogen and the fibre present.

Substance.	Nitrogen in precipitate by bromine.	Proteids (N × 6.25).
Liebig Company's extract	1.41 per cent.	8.92 per cent.
Seasoned bovril	1.94 "	12.28 "
Bovril for invalids	2.64 "	16.71 "

Koenig and Boemer have shown that the proteid nitrogen in meat extracts is generally much over-estimated. They found a total of 1.17 per cent of proteid nitrogen in the Liebig Company's extract, which is equivalent to 7.41 per cent of total proteids, mostly albumose. The fact that bromine completely precipitates all proteid and gelatinoid matters in solution, affords a convenient means of solving certain problems which have hitherto presented considerable difficulty. For instance, in a solution which has been subjected to digestion it may be possible to precipitate all the unchanged proteids by saturation with zinc sulphate. The peptones which have been formed during digestion remain in solution and can be separated by filtration. In the filtrate the peptones can be completely precipitated by bromine, and thus the total quantity of

these bodies formed during digestion can be accurately determined.

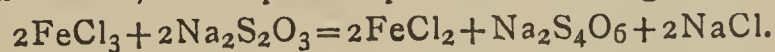
Allen and Searle applied this method to an examination of the Liebig Company's extract, 5 grms. of which were dissolved in 100 c.c. of water and the solution saturated with zinc sulphate. After filtering, bromine water was added to the filtrate and a precipitate produced which redissolved on diluting with water and the addition of hydrochloric acid. When the filtrate from the saturated zinc sulphate was previously diluted with water and acidulated, no precipitate was formed on the addition of bromine. This reaction shows that no considerable quantities of real peptones exist in Liebig's extract.

Since this bulletin was prepared for the press, an extensive article on the halogen derivatives of albumen has been published by F. Blum and W. Vaubel of Frankfurt, Germany ("Ueber Halogeneiweissderivate," *Journ. für Praktische Chemie*, 1897, lxvi., 393—6, and 1898, lvii., 365—396).

THE ESTIMATION OF IRON IN THE FERRIC STATE BY REDUCTION WITH SODIUM THIOSULPHATE AND TITRATION WITH IODINE.*

By JOHN T. NORTON, Jun.

THE action of sodium thiosulphate on ferric iron has long been known, and depends upon the following reaction:—



As early as 1859, Sherer (*Gelehrte Anzeigen der König. Bayrisch. Acad.* vom Aug. 31, 1859) proposed a method for the estimation of ferric iron depending on the above reaction. Sherer's method of procedure was to act upon a solution of ferric chloride with sodium thiosulphate until the purple colour produced by the interaction of these two salts just vanished. Mohr's (*Anal. d. Chem. u. Pharm.*, cxiii., 260) experimental tests of this process were not successful. A year or two later, Kremer and Landolt (*Zeit. Anal. Chem.*, i., 214), after a careful investigation of Sherer's process, recommended it with the modification that any free hydrochloric acid present should be neutralised by sodium acetate until the solution assumed a red colour, just enough hydrochloric acid added to destroy this red colour, and sodium thiosulphate run into the solution in slight excess. When the liquid became perfectly colourless and gave no reaction for ferric iron with potassium sulphocyanide, the excess of sodium thiosulphate was titrated back with iodine and starch. The authors also state that the ferric iron should not be present in concentrated solution. Very good results were claimed for this process, but it apparently gained but slight recognition.

Oudemans (*Zeit. Anal. Chem.*, vi., 129), who was the next to study the action of ferric iron and sodium thiosulphate, claimed that the addition of a small quantity of cupric salt to the iron solution hastened the reducing action of the sodium thiosulphate. Mohr ("Titrimethode"), however, condemned this method also as unreliable, both because the sodium thiosulphate acted upon the copper as well as the iron and also because the potassium sulphocyanide, added as an indicator of the completeness of the reduction, produced a precipitate of cupric sulphocyanide which interfered with the reaction. In a second paper, Oudemans (*Zeit. Anal. Chem.*, ix., 362) reiterated his former statement as to the accuracy of his method, but advised the use of a smaller quantity of the cupric salt. An improvement on Oudemans's process was proposed by Haswell (*Repertorium der Analytischen Chem.*, i., 179), who mixed the moderately acid solution

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, viii., July, 1899.

of ferric chloride in the presence of a cupric salt with a few drops of sodium salicylate and then reduced with sodium thiosulphate previously standardised upon a known quantity of iron by the same process, and estimated the excess by potassium dichromate. Bruel (*Comptes Rendus*, xcvi., 954) modified this process by operating without the copper solution, relying merely on the discharge of the violet colour in a boiling solution by sodium thiosulphate standardised on a ferric solution of known strength.

Although considerable work has been done on the reaction between ferric iron and sodium thiosulphate, no process depending upon this reaction has obtained acceptance. In view, therefore, of previous work on the action of hydrochloric acid upon sodium thiosulphate (*American Journal of Science*, vii., 287; *CHEM. NEWS*, lxxx., p. 27), and with the idea that a careful control of the dilution and quantity of acid present might greatly better the accuracy of the method, it has seemed to me to be desirable to study this process again in detail.

The ferric oxide employed in the experiments was prepared with great care by the ignition of ferrous oxalate obtained by acting with oxalic acid on pure ammonium ferrous sulphate. To ascertain, however, if this oxide contained any impurity, about 0.5 of a gram. was put into a porcelain boat and submitted to the action of a current of hydrochloric acid gas and chlorine at a temperature of about 280° C.—according to a process recently described from this laboratory (Gooch and Havens, *Am. Journ. Sci.*)—until all the ferric salt is volatilised in the form of ferric chloride. A residue of 0.0010 gram. for every 0.5 of a gram. of the oxide was found, and this correction, small for the amounts generally used, has been applied in the following determinations. The sodium thiosulphate used was taken in nearly $n/10$ solution, and was standardised against an approximately decinormal solution of iodine which had been determined by comparison with decinormal arsenious acid made from carefully re-sublimed arsenious oxide.

In those experiments which deal with amounts of ferric oxide not exceeding 0.2 of a gram., measured portions of a solution of ferric chloride made of known strength by dissolving about 2 grms. of the pure carefully weighed ferric oxide in 20 c.m.³ of strong hydrochloric acid and diluting to 1 litre, were drawn from a burette. In the case of the larger quantities of ferric oxide the salt was weighed out, dissolved in hydrochloric acid, and brought to the required dilution. The ferric chloride, either drawn from the burette or prepared directly from the weighed oxide, was diluted with water, a drop of potassium sulphocyanide added to serve as an indicator, and an excess of sodium thiosulphate was run in until, after standing for a few minutes, the solution became perfectly colourless, and the excess of sodium thiosulphate was then titrated back with decinormal iodine after the addition of starch.

Several sources of error are plainly possible in the process: incompleteness in the reduction of the ferric salt; decomposition of the thiosulphate by the acid, resulting in the subsequent over-run of iodine; the possible tendency of the ferric salt under concentration to oxidise the thiosulphate to the condition of the sulphate rather than to that of the tetrathionate; and, finally, the oxidising action of the air, which may tend to keep up progressive oxidation of the iron salt and excessive expenditures of thiosulphate. The first three sources of difficulty tend to produce errors of deficiency; the fourth an error of excess.

The first step in the experimental study of the process was to determine the effect of varying dilution upon the estimation of a given quantity of iron reduced by sodium thiosulphate, taken in practically uniform excess above the amount theoretically required, in the presence of 1 c.m.³ of hydrochloric acid.

This table shows plainly that with quantities of ferric oxide present up to 0.1 gram. the dilution can vary from 400 c.m.³ to 1000 c.m.³ for each c.m.³ of strong hydro-

chloric acid and still give excellent results. At a dilution greater than 1000 c.m.³ the action of the thiosulphate is evidently incomplete, and at a smaller dilution than 400 c.m.³ the decomposing action of the acid on the thiosulphate becomes noticeable. When larger quantities of iron oxide are dealt with, it appears that the dilution ought to be increased proportionally with the quantity of ferric oxide present as well as with that of the acid. This is illustrated in Experiments 9—15 of the table. On this account it seems necessary, assuming that the quantity of acid present is always kept within the maximum strength mentioned (1 c.m.³ to 400 c.m.³), to regulate the dilution from the approximate quantity of the iron so that not less than 400 c.m.³ of water shall be used to every 0.1 gram. of iron oxide present. Under properly regulated conditions of dilution as regards acid and the iron salt, the reduction is completed in from five to ten minutes.

TABLE I.

	Fe ₂ O ₃ taken. Grm.	Fe ₂ O ₃ corrected. Grm.	Dilu- tion. C.m. ³ .	HCl. C.m. ³ .	Na ₂ S ₂ O ₃ in excess. C.m. ³ .	Fe ₂ O ₃ found. Grm.	Error. Grm.
1.	0.1000	0.0998	100	1	18.08	0.0957	0.0041—
2.	0.1000	0.0998	200	1	20	0.0966	0.0032—
3.	0.1000	0.0998	300	1	17.56	0.0995	0.0003—
4.	0.1000	0.0998	400	1	17.16	0.0998	0.0000
5.	0.1000	0.0998	600	1	17.76	0.0996	0.0002—
6.	0.1000	0.0998	800	1	17.65	0.0993	0.0005—
7.	0.1000	0.0998	1000	1	18.02	0.0988	0.0010—
8.	0.1000	0.0998	1200	1	17.95	0.0977	0.0021—
9.	0.1000	0.0998	1400	1	17.99	0.0965	0.0033—
10.	0.1000	0.0998	1600	1	18.01	0.0947	0.0051—
11.	0.2001	0.1997	400	2	27.05	0.2029	0.0032+
12.	0.2001	0.1997	800	2	15.95	0.1998	0.0001+
13.	0.4998	0.4988	1000	2	22.36	0.5104	0.0126+
14.	0.5051	0.5041	1800	4	15.27	0.5026	0.0017—
15.	0.4002	0.3994	1500	4	27.29	0.3996	0.0002+
16.	0.7502	0.7487	1000	1	9.73	0.7572	0.0085+
17.	0.7029	0.7015	2000	4	12.67	0.7004	0.0011—

Great excesses of acid, however, contrary to the statement of Kremer (*Zeit. Anal. Chem.*, i., 214), retard the reduction greatly, and, in spite of the tendency of the thiosulphate to decomposition and the production of errors of deficiency under such circumstances, plus errors due to partial oxidation come to light. This fact appears in the following table, which records the results of processes lasting many hours.

TABLE II.

	Fe ₂ O ₃ taken. Grm.	Fe ₂ O ₃ corrected. Grm.	Dilu- tion. C.m. ³ .	HCl. C.m. ³ .	Na ₂ S ₂ O ₃ in excess. C.m. ³ .	Fe ₂ O ₃ found. Grm.	Error. Grm.
18.	0.5012	0.5002	1700	10	25.99	0.5308	0.0306+
19.	0.7512	0.7497	1200	15	57.8	0.7685	0.0188+
20.	0.7520	0.7505	2000	15	56.4	0.7983	0.0478+
21.	0.7520	0.7505	1700	15	27.2	0.7627	0.0122+

As to the temperature at which the reduction should be made, my experience, contrary to that of Kremer, goes to show that no elevation above atmospheric conditions is necessary; under the conditions of acidity and dilution laid down, the process of reduction is complete within ten minutes after the introduction of the thiosulphate; moreover, former experience (*Am. Journ. Sci.*, vii., 287) shows clearly the danger of submitting mixtures of sodium thiosulphate and acid to temperatures much above the ordinary. On the other hand, artificial reduction of temperature tends to retard the action to an impossible degree. Thus, in an experiment it took five minutes to reduce 0.0500 of ferric oxide at 21° C. completely at a dilution of 200 c.m.³ and in the presence of $\frac{1}{2}$ c.m.³ of hydrochloric acid; under conditions otherwise precisely similar, excepting that the temperature was lowered to 0° C., the action lingered forty-five minutes.

Lastly, the question as to the excess of thiosulphate

necessary to complete the reduction within a reasonable time must be considered. In nearly all previously recorded experiments the excess of thiosulphate was not less than 15 c.m.³ of the *n*/10 solution. The following table shows the effect of diminishing this excess.

TABLE III.

	Fe ₂ O ₃ taken. Grm.	Fe ₂ O ₃ corrected. Grm.	Dilu- tion. C.m. ³ .	HCl. C.m. ³ .	Na ₂ S ₂ O ₃ in excess. C.m. ³ .	Fe ₂ O ₃ found. Grm.	Error. Grm.
22.	0.0250	0.0250	400	$\frac{1}{4}$	12.2	0.0241	0.0009—
23.	0.0500	0.0499	400	$\frac{1}{2}$	12.2	0.0495	0.0004—
24.	0.0500	0.0499	400	$\frac{1}{2}$	13.66	0.0493	0.0006—
25.	0.1000	0.0998	400	1	7.31	0.0984	0.0014—
26.	0.1000	0.0998	400	1	7.63	0.0972	0.0026—
27.	0.1001	0.0999	400	1	12.88	0.1007	0.0008+
28.	0.1498	0.1495	600	$1\frac{1}{2}$	11.97	0.1475	0.0020—
29.	0.1996	0.1992	800	2	12.43	0.1980	0.0012—

From the above experiments, taken in connection with those of Table I., it is clear that there should always be present an excess of at least 15 c.m.³ of the *n*/10 solution of sodium thiosulphate. If the quantity of hydrochloric acid is kept very low there is no reason why this excess of thiosulphate could not be considerable without producing any disturbing effect. Practically, however, the presence of an excess between the limits of 15 c.m.³ and 35 c.m.³ of the *n*/10 solution has been found to give the most satisfactory results.

To recapitulate, then, it has been shown that the dilution must be at least 400 c.m.³ for each 0.1 of a gram. of iron oxide present, that the quantity of acid should never exceed 1 c.m.³ of the strong acid to each 400 c.m.³ of water, that the time of reduction must be short to avoid progressive oxidation, that the temperature of the solution should be kept at the normal temperature of the atmosphere, and finally that the excess of sodium thiosulphate present should never be less than 15 c.m.³ of the *n*/10 solution. In the case of large dilution the use of freshly-boiled water is recommended, so as to avoid the re-oxidising effect of the air upon the reduced iron. In the experiments included in the following table, the above precautions were closely adhered to and manifestly satisfactory results were obtained.

TABLE IV.

	Fe ₂ O ₃ taken. Grm.	Fe ₂ O ₃ corrected. Grm.	Dilu- tion. C.m. ³ .	HCl. C.m. ³ .	Excess Na ₂ S ₂ O ₃ . C.m. ³ .	Fe ₂ O ₃ found. Grm.	Error. Grm.
30.	0.0125	0.0125	200	$\frac{1}{8}$	23.5	0.0125	0.0000
31.	0.0250	0.0250	400	$\frac{1}{4}$	21.98	0.0250	0.0000
32.	0.0250	0.0250	400	$\frac{1}{4}$	17.	0.0250	0.0000
33.	0.0250	0.0250	400	$\frac{1}{4}$	17.	0.0250	0.0000
34.	0.0500	0.0499	400	$\frac{1}{2}$	24.	0.0498	0.0001—
35.	0.0500	0.0499	400	$\frac{1}{2}$	19.	0.0498	0.0001—
36.	0.0500	0.0499	400	$\frac{1}{2}$	15.1	0.0497	0.0002—
37.	0.0500	0.0499	400	$\frac{1}{2}$	19.	0.0498	0.0001—
38.	0.1001	0.0999	400	1	23.1	0.0993	0.0006—
39.	0.1001	0.0999	400	1	17.93	0.0997	0.0002—
40.	0.1001	0.0999	400	1	22.92	0.0997	0.0002—
41.	0.1001	0.0999	400	1	18.	0.0997	0.0002—
42.	0.1001	0.0999	400	1	16.	0.0996	0.0003—
43.	0.1498	0.1495	600	$1\frac{1}{2}$	23.26	0.1493	0.0002—
44.	0.1498	0.1495	600	$1\frac{1}{2}$	16.66	0.1493	0.0002—
45.	0.1498	0.1495	600	$1\frac{1}{2}$	26.87	0.1475	0.0020—
46.	0.1996	0.1992	800	2	22.38	0.1990	0.0002—
47.	0.1996	0.1992	800	2	17.29	0.1999	0.0007+
48.	0.1996	0.1992	800	2	22.20	0.1991	0.0001—
49.	0.4045	0.4037	1600	4	16.03	0.4042	0.0005+
50.	0.4045	0.4037	1600	4	16.2	0.4023	0.0014—
51.	0.4018	0.4010	1600	4	16.34	0.4007	0.0003—
52.	0.5051	0.5041	1800	4	15.27	0.5026	0.0015—

As seen in the table, this process is very accurate—especially in the use of small amounts of ferric oxide. The introduction of cupric sulphate, as recommended by Oudemans, or of sodium salicylate according to Has-

well's method, seems to be unnecessary and only complicates the process.

In treating ferric oxide, the following method of procedure is recommended:—Dissolve an amount not exceeding 0.2 gram. of the oxide in hydrochloric acid, evaporate to a pasty mass, dilute to about 800 c.m.³ with freshly-boiled water, add a drop of potassium sulphocyanide, and into this solution run 50 c.m.³ of approximately *n*/10 sodium thiosulphate; allow the liquid to stand until perfectly colourless, and determine the excess of thiosulphate by *n*/10 iodine and starch. For quantities of iron oxide up to 0.2 of a gram. this process is quick and most accurate; when care is taken to preserve the relations of acidity and dilution, twice the amount of ferric oxide mentioned above may be handled.

In conclusion, I wish to thank Prof. F. A. Gooch for his kind advice and many suggestions.

THE TITRATION OF OXALIC ACID BY POTASSIUM PERMANGATE IN PRESENCE OF HYDROCHLORIC ACID.*

By F. A. GOOCH and C. A. PETERS.

(Concluded from p. 80).

As Kessler has noted, a sufficiency of the manganous salt, acting no doubt as the medium of transfer of oxygen, may bring about interaction between the permanganate and the oxalic acid at atmospheric temperatures without the tedious delay ordinarily encountered in the attempt to consummate that action in cold solutions. It would seem natural that the manganic hydroxide formed in the Guyard reaction at low temperatures should yield more readily to the reducing action of the oxalic acid than the more anhydrous form to be expected in hot solutions, so that at such temperatures the limits as to proportions of manganous salt, acid, and dilution, within which favourable action may take place, should be wider; moreover, the undesirable action of the permanganate upon hydrochloric acid, when that acid is present, should be less appreciable at lower temperatures. In our experiments, therefore, upon the oxidation of oxalic acid by potassium permanganate in presence of hydrochloric acid, we have studied the effect of varying the proportions of the manganous salt both at atmospheric temperatures and the higher temperatures generally employed.

From these results (Table IV.) it appears that the presence of a suitable amount of manganous salt—either the sulphate (Experiments 4—7, 13—15, 22—24) or the chloride (Experiments 10—12, 16—20)—is capable, either in cold solution (Experiments 1—20) or in hot solution (Experiments 22—24) of preventing the action of the permanganate upon the hydrochloric acid. It appears, also, that, for a given dilution and strength of acid, less manganous salt is needed in the cold solution (Experiments 4—7) than in the hot solutions (Experiments 22—24). Thus, in the hot solution, at a dilution of 145 c.m.³ to 500 c.m.³, 1 gram. of manganous sulphate must be present with 5 c.m.³ of strong hydrochloric acid, with or without sulphuric acid; while in the cold solution 0.04 gram. of either the sulphate or chloride is enough to secure adequate protective effect. Experience showed, however, that 0.5 gram. or 1.0 gram. of the manganous salt should be present in order to push the reaction with reasonable speed in cold solutions.

Wagner (*loc. cit.*) has made record of the increased evolution of chlorine in oxidations of ferrous chloride by potassium permanganate in presence of various salts, of which barium chloride was the most active. We have made some experiments, therefore, to determine whether

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, Fourth Series, vol. vii., June, 1899.

TABLE IV.
(Temperature 20—26° C.).

Number of experiment.	Volume at beginning of titration.	H ₂ SO ₄ . 1 : 1. C.m. ³ .	HCl. Sp. gr. 1.09. C.m. ³ .	Ammonium oxalate. 1/10 N. C.m. ³ .	KMnO ₄ . C.m. ³ .	MnSO ₄ 5H ₂ O. Grms.	MnCl ₂ 4H ₂ O. Grms.	Variation from standard. C.m. ³ .
1.	130	—	10	25	23.90	0.0040	—	+0.15
2.	130	—	10	25	23.90	0.0120	—	+0.15
3.	130	—	10	25	23.80	0.0250	—	+0.05
4.	130	—	10	25	23.75	0.0400	—	+0.00
5.	130	—	10	25	23.76	0.0500	—	+0.01
6.	130	—	10	25	23.70	0.1000	—	-0.05
7.	130	—	10	25	23.75	0.2000	—	0.00
8.	130	—	10	25	24.20	—	0.0200	+0.45
9.	130	—	10	25	23.95	—	0.0200	+0.20
10.	130	—	10	25	23.80	—	0.0400	+0.05
11.	130	—	20	25	23.75	—	0.0400	0.00
12.	130	—	30	25	23.75	—	0.0400	0.00
13.	130	—	10	25	23.75	1.0000	—	0.00
14.	130	—	10	25	23.75	2.0000	—	0.00
15.	130	—	10	25	23.75	3.0000	—	0.00
16.	130	1	—	25	23.72	—	1.0000	-0.03
17.	130	1	—	25	23.74	—	2.0000	-0.01
18.	130	1	—	25	23.72	—	3.0000	-0.03
19.	130	2	—	25	23.70	—	0.5000	-0.05
20.	130	3	—	25	23.75	—	0.5000	0.00
(Temperature about 80°).								
21.	145	10	10	25	23.90	0.5000	—	+0.15
22.	145	10	10	25	23.70	1.0000	—	-0.05
23.	500	10	10	25	23.75	1.0000	—	0.00
24.	500	—	10	25	23.70	1.0000	—	-0.05
25.	500	—	10	25	24.10	0.5000	—	+0.35

TABLE V.

(Volume at beginning of titration = 140 c.m.³. Temperature = 20—24° C.).

Ammonium oxalate. C.m. ³ .	HCl. Strongest. C.m. ³ .	MnCl ₂ 4H ₂ O.	BaCl ₂ . Grms.	SrCl ₂ . Grms.	CaCl ₂ . Grms.	MgCl ₂ . Grms.	KMnO ₄ used. C.m. ³ .	Error. C.m. ³ .
25	5	0.5	—	—	—	—	26.05	0.00
25	5	—	—	—	—	—	27.45	+1.40
25	5	—	2	—	—	—	26.50	+0.45
25	5	—	—	2	—	—	26.53	+0.48
25	5	—	—	—	2	—	26.36	+0.35
25	5	—	—	—	—	2	26.13	+0.08
25	5	0.5	2	—	—	—	26.05	0.00
25	5	0.5	—	2	—	—	26.10	+0.05
25	5	0.5	—	—	2	—	26.10	+0.05
25	5	0.5	—	—	—	2	26.05	0.00
25	10	1.0	2	—	—	—	26.10	+0.05
25	10	1.0	—	2	—	—	26.05	0.00
25	10	1.0	—	—	2	—	26.06	+0.01
25	10	1.0	—	—	—	2	26.11	+0.06

such action would appear in the oxidation of oxalic acid in cold solutions containing certain salts, and, if so, whether it would be preventable by the presence of the manganous salt under our conditions of working. From the results given in Table V., it is plain that the evolution of chlorine in cold solutions is less in the presence of these salts than when hydrochloric acid is used without them, and that such evolution may be entirely prevented (within the proportions of our work) by the presence of 0.5 gram. to 1 gram. of manganous chloride.

Finally, it appears as the result of an investigation, that the titration of oxalic acid by potassium permanganate in presence of hydrochloric acid is ordinarily attended with some inaccuracy due to liberation of chlorine from the hydrochloric acid; that this tendency may be overcome by the presence of a manganous salt (either the sulphate or chloride); that 1 gram. of the manganous salt is enough to so affect the conditions of equilibrium that

titrations in moderate volumes (100 c.m.³ to 500 c.m.³) and in presence of hydrochloric acid (5 c.m.³ to 15 c.m.³ of the strong acid) may be conducted with safety and reasonable rapidity, either with or without sulphuric acid, at the ordinary atmospheric temperature.

ON THE CLAIMS OF DAVY^{UM} TO RECOGNITION AS A CHEMICAL ELEMENT.*

By J. W. MALLET.
(Concluded from p. 81).

THE crude common salt in rose-coloured crystals dissolved almost completely in water, producing a solution of rather orange or aurora-red colour, having a distinct,

* From the *American Chemical Journal*, Vol. xx., No. 9.

though not very strong, acid reaction to litmus. Using a minimum quantity of cold water, applied in several successive portions, a minute residue was left undissolved, but a few m.grms. from a couple of hundred grms. of the salt, which residue consisted partly of fine light grey matter resembling that already noticed, but chiefly of a buff-coloured powder, appearing under the microscope (with a power of 250—450 diameters) as distinctly transparent and crystalline, with the general aspect of minute octahedra and cubo-octahedra; no colours shown in polarised light. The clear aqueous solution was reduced by a rod of extremely pure zinc and a little hydrochloric acid. Most of the metallic precipitate thrown down was loose and flocculent, but there was a strong tendency to the formation of a *specular* and pretty firmly adherent deposit on the glass of the beaker and stirring-rod. The precipitate, dried at 120° C., represented a little less than 0.2 per cent of the crude salt taken. This precipitate, which if strongly ignited in the air gave off a slight but unmistakable odour of osmium tetroxide, was re-dissolved by *aqua regia*, and the solution was mixed with a moderate excess of sodium chloride, evaporated almost to dryness, re-diluted with water, and again evaporated to remove surplus acid, and finally allowed to stand in the cold for two or three days, the concentration being such that only a little sodium chloride separated out. On decanting, and cautiously removing by water the small remaining surplus of sodium chloride, a little more of a buff-coloured residue was obtained, looking, both to the naked eye and under the microscope, like the original residue from the treatment of the crude rose-coloured salt with water. The buff-coloured material from these two sources—that first obtained having been freed from the light grey powder by washing with a saturated solution of common salt, and decantation—was washed with alcohol, in which it seemed to be practically insoluble, and dried. A little specimen of it dissolved in a large quantity of water. Another small portion, tested spectroscopically, showed the presence of sodium with a trace of potassium. The principal part was dried at 120° C., weighed, and heated to redness in a stream of hydrogen; the residual metal, washed free of alkaline chloride, was dried and weighed; it formed 37.1 per cent of the salt decomposed. Assuming this double chloride to be anhydrous, sodium to be the only alkaline metal present, and a single metal of the platinum group to be associated with it, the atomic mass of such platinum metal would be 151.5 for the formula Na_2MCl_6 , or 165 for the formula Na_3MCl_6 . Of these formulæ the former is the more probable, and leads to an approximate value for the atomic mass not very different from that assigned by Kern to davyum. Both determinations were made with quantities altogether too small for any very accurate result.

The general properties of the metallic material thus obtained agreed in the main with those described by Kern, as far as they could be compared by experiments on so minute a scale, and after solution in *aqua regia*, which was effected but slowly and with difficulty, the reactions in the liquid way were pretty nearly such as he obtained. But, although a small part of the solution gave a red colouration with potassium thiocyanate, a reaction pointed out by Kern as among those particularly characteristic of davyum, a simple additional test with potassium ferrocyanide at once showed the presence of iron, though in small amount, thus accounting for the red colour. Furthermore, on placing, in the chief portion of the solution, a little lump of sal ammoniac and allowing it to remain until it had dissolved to saturation, a dark brown-red precipitate was formed, from which the ordinary reactions of iridium were obtained, while the remaining liquor, evaporated to dryness and the solid residue ignited, left rhodium, probably not pure, but identifiable by the action upon it of fused potassium acid sulphate; so that the material examined consisted, not of a single distinct metal, but merely of a mixture of iridium and rhodium with a little iron. The whole quantity available was

quite insufficient for any exact quantitative analysis, but the very rough approximation to a mean atomic mass indicates that the two metals of the platinum group must have been present in not very unequal quantities.

Of course the results thus obtained, while lending no support to a belief that there is such an element as davyum, do not suffice to disprove its existence. It may, however, be remarked that in the account given by Kern himself of his experiments, there are some points tending to increase doubt as to the conclusion which he reached. Thus there is, probably from carelessness, some erroneous statement of facts, as, for instance, the assertion that *like platinum chloride* the chloride of davyum forms double salts with ammonium and potassium chlorides *insoluble in water and easily soluble in absolute alcohol*. It is suggestive that davyum is said to have been obtained from native platinum in the separation of rhodium and iridium. There is no allusion to the well-known fact of the reactions afforded by one of the platinum metals being modified by the presence along with it of others of this group, notably true of iridium solutions when containing also platinum, palladium, or rhodium. It is unsatisfactory to find the statements that "careful qualitative analyses showed no presence whatever of iron," and that the author's davyum "was found to contain no metals of other groups" without any details being given of the tests by which it was supposed that these points were established.

On the whole it seems most probable that, in default of better proof of elementary character than has yet been given, davyum is to be looked upon as merely a mixture of iridium and rhodium with a little iron; and, hence, that we have not yet reason to believe in the existence of a third triad group of platinum metals.

SEVENTEENTH ANNUAL REPORT OF THE COMMITTEE ON INDEXING CHEMICAL LITERATURE.*

THE Committee on Indexing Chemical Literature respectfully presents to the Chemical Section its Seventeenth Annual Report, covering the twelve months ending August, 1899.

Works Published.

"A Select Bibliography of Chemistry, 1492—1897." By Henry Carrington Bolton. First Supplement. Smithsonian Miscellaneous Collections 1170. City of Washington, 1899. Pp. x.+489. 8vo.

This work includes titles omitted in the volume published in 1893, and brings the literature down to 1897, the plan and scope being the same. In collecting the 5554 titles the author had the co-operation of eminent men of science and letters in several parts of the world.

"Index to the Literature of Thallium, 1861—1897." By Miss Martha Doan.

This is passing through the press, and will probably be issued before this Report is presented to the Section. It will form one number of the Smithsonian Miscellaneous Collections.

Works in Preparation and Reports of Progress.

"Index to the Literature of Zirconium." By A. C. Langmuir and Charles Baskerville.

The manuscript has been critically examined by each member of the Committee and unanimously recommended to the Smithsonian Institution for publication.

"A Select Bibliography of Chemistry, 1492—1897." Second Supplement. By Henry Carrington Bolton.

* Advance proofs from the *Proceedings of the American Association for the Advancement of Science*, Columbus Meeting, 1899.

The manuscript of this work, which embraces Chemical Dissertations only, has been completed and presented to the Smithsonian Institution.

"A Bibliography of Malonic Acid and its Derivatives" has been begun by Dr. Thomas Clarke, University of North Carolina.

A Third Supplement to the "Select Bibliography of Chemistry" has been commenced by Dr. H. Carrington Bolton.

"Science Abstracts." The Physical Society of London published in 1895-1897 three volumes of "Abstracts of Physical Papers from Foreign Sources," edited by Mr. J. Swinburn. Each volume has author and subject indexes. Since January, 1898, these abstracts have appeared monthly in enlarged scope under the title "Science Abstracts: Physics and Electrical Engineering." Issued under direction of the Institution of Electrical Engineering and the Physical Society of London. J. Swinburn, Editor. Monthly. Spon and Chamberlain, Agents, New York.

This important undertaking includes electrochemistry and chemical physics. The editor is assisted in his work by W. R. Cooper and a corps of fifty-two abstractors.

Committee:—

H. CARRINGTON BOLTON, Chairman,
F. W. CLARKE,
A. R. LEEDS,
A. B. PRESCOTT,
ALFRED TUCKERMAN,
H. W. WILEY.

OBITUARY.

PROF. ROBERT WILHELM BUNSEN.

It is with sincere regret that we have this week to record the death of another of the most distinguished chemists of the century, in the person of Professor Bunsen, who died at Heidelberg on the 16th of this month, at the ripe age of 88.

Prof. Bunsen was born on the 13th March, 1811, at Göttingen, where his father was Professor of Occidental Literature. He studied Science at that University, and after continuing his education at Paris, Berlin, and Vienna, he took his degree in 1833. In 1836 he succeeded Wöhler as Professor of Chemistry in the Polytechnic Institution at Cassel, and in 1838 was appointed Assistant-Professor in the University of Marburg. Three years later he was made Titular Professor, and then became Director of the Chemical Institute; he also held several other appointments.

His great work dates back to 1856, when he shared with Professor Kirchhoff the discovery of spectroscopic astronomy, on which our knowledge of the chemical constituents of the sun and stars has been built up. It is widely thought that the chief merit for the discovery of spectrum analysis should be awarded to Bunsen. Amongst his numerous other discoveries we may mention the battery and burner which bear his name. He was also the author of many scientific works, and had received several honorary degrees from Universities throughout Europe. In 1833 he was appointed one of the eight Foreign Associates of the Paris Academy of Sciences.

We take the following from a notice of Professor Bunsen which appeared in *The Times* of the 17th inst.:—

Full of years—he was born in 1811—and full of honours, he has passed to his rest after a long life exclusively devoted to the prosecution of his science. The

latter years of his life were passed in retirement at Heidelberg. He retained his faculties to the end of his days, and even in his 88th year, though his hearing was somewhat impaired, the chief complaint he had to make to an English visitor was that he was beginning to find that his eyesight was not so good as it used to be. With his death the last link is severed between the great German scientists of the past and their followers of to-day, who endeavour—with what success may be a matter of opinion—to walk in the footsteps of their scientific forbears. To each of these, all the world over, the death of Bunsen comes as a personal grief. For none, not even Liebig or Hofmann, have left behind them such warm and affectionate memories as those which cluster round the name of the great investigator and teacher whose hand and voice are now stilled.

The son of a distinguished Göttingen theologian, Bunsen was brought up from his earliest days in a University atmosphere, and soon showed that power of keen observation and manipulative dexterity which placed him for long years in the forefront of modern experimental philosophers. The facts of his life may be shortly stated. Born in 1811, he graduated at Göttingen University as Ph.D. in 1831. After spending a few years in study at Paris, Berlin, and Vienna, in 1836 he succeeded Wöhler as Professor of Chemistry in the Polytechnic School at Cassel. Two years later he went to Marburg; then, in 1852, after a short interval at Breslau, he was appointed to the chair of experimental chemistry at Heidelberg, where he remained, in spite of a tempting invitation to Berlin University, until his resignation in 1889. Many academical distinctions of course fell to his share, both in his own country and abroad. In England the Royal Society—which in 1858 elected him one of its foreign members—awarded him the Copley medal in 1860, and seventeen years afterwards chose him and his fellow-worker Kirchhoff to be jointly the first recipients of the newly-instituted Davy medal.

As a "privat docent" in his native University, he first showed his ability in the prosecution of a difficult and dangerous investigation upon a series of poisonous and explosive organic compounds of arsenic, and in the course of these experiments he met with an accident which nearly cost him his life, but, undaunted, he pursued his work until he succeeded in placing the chemistry of the whole subject in a clear light. To enumerate the discoveries in almost every branch of chemistry made by his unwearied assiduity would fill a treatise. Suffice it here to enumerate those which have made Bunsen's name a household word. First came the Bunsen voltaic-battery, which, supplanting the more expensive form bearing the name of our countryman Grove, was generally used as the cheapest and most effective mode of generating electricity until the dynamo displaced all forms of chemical batteries. Next came the Bunsen gas burner, which, it is not too much to say, is now not only a necessity in the laboratory, but in every household and every manufactory where a clean flame is wanted. About his discovery of this simple and effective apparatus an interesting tale could be told. No one before Bunsen had thought it possible that a mixture of coal-gas and air could be made to burn without explosion from a simple tube-burner. His clear conception of the laws which apply to the inflammation of such a mixture showed him that it was possible to arrange the dimensions in such a way that a steady, smokeless, and highly combustible mixture could be obtained, but a long series of delicate experiments was needed before the perfect burner which now bears his name resulted. Of other investigations carried out by Bunsen may be mentioned those on the chemistry of blast-furnace gases, in conjunction with the late Lord Playfair, on actinometry and the chemical action of light with Sir Henry Roscoe, and on the geological conditions of Iceland and the theory of the geysers—the result of a visit to that island in 1847.

The research, however, by which, perhaps, more than

any other the name of Bunsen will go down to posterity, linked with that of his colleague Kirchhoff, is the discovery of spectrum analysis, for this opened out a field of experiment so new and so vast that it may well be said to be the most important scientific result accomplished during the latter half of the century, a time pregnant with work of a truly marvellous character. To have added a new branch to Chemical Science which throws a clear and wholly unexpected light upon the constitution of terrestrial matter, which has been the means of discovering many new chemical elements, and of proving the widespread distribution of others hitherto considered as rare, would in itself have been a work of primary significance; but when to that is added the fact that by means of this far-reaching method the bounds of our planet are outstepped and a knowledge not only of the chemical composition of the sun and of the far-distant stars, but even of their rates of motion, have thus been obtained, an idea may be formed of the debt of gratitude which all interested in human progress must feel to the two great twin brethren who in their quiet laboratory at Heidelberg revealed such hidden secrets. But these, though the best-known and most popular of the achievements of the Heidelberg master, are not more important from a scientific point of view than many others all known and valued by the chemist and physicist. To have first instituted methods of almost astronomical precision in the measurement and separation of gases, and thus to have laid on a firm foundation the branch science of gas analysis, is in itself sufficient to have marked him as one of the first experimentalists of the age. Add to that his numerous memoirs on purely chemical subjects, all marked by the same accurate work: add again his researches in physical chemistry; on the measurement of the chemical action of light—carried on in conjunction with one of his pupils—and, again, one on a new and improved method of determining specific heat, not forgetting his chemico-geological researches which constitute what may well be termed an epoch-making discovery as to the composition of the volcanic rocks of our planet,—and it is not too much to say that for variety and importance the theoretical and experimental work proceeding from his brain and hands has rarely, if ever, been exceeded.

This work, although great, is by no means the only, or even the greatest, work achieved by Bunsen. He has built up a vast and enduring reputation by his labours as a teacher and as a master craftsman. Passionately devoted to his laboratory and to his students, he formed a school of chemistry second only—and about that there may be a question—to that of Liebig at Giessen. His lectures were original and most instructive, but it was in the patient teaching in the laboratory that his genius showed itself strongest, and the pupils from all parts of the world who were fortunate enough to work under him in his most prolific days in Heidelberg all conceived for him the deepest feelings of respect and affection, his precept and example having influenced their whole lives. Those who had the privilege of intimate association with him knew him as the best and most reliable and most affectionate of friends. His presence was always welcomed in the academic circles of his University, for his simple and original nature—disliking show and despising pretence—exhibited in such society a fund of quiet humour which gave a special zest to his presence and conversation. Amongst his academic colleagues no one was honoured as he. Orders and decorations from all parts were his by the score; but these he valued less than the recognition by his brother men of science of the work he had done as typified by election as member of scientific societies, and amongst these he always placed in front rank that of the foreign Fellowship of our Royal Society.

Sodium Persulphate as a Germicide.—Friedlaender (*Pharm. Centralhalle*) reports favourably on the antiseptic and germicidal properties of sodium persulphate, $\text{Na}_2\text{S}_2\text{O}_8$.

CHEMICAL NOTICES FROM FOREIGN SOURCES

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

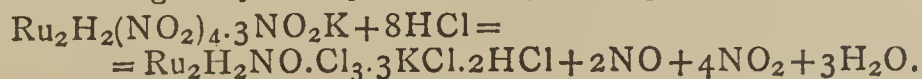
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 4, July 24, 1899.

Isomeric Forms of Chromic Acetate.—A. Recoura.—In a preceding paper the author announced that he had established the existence of four isomeric forms of chromic acetate, $\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_3$. The normal acetate is an ordinary metallic salt, of a lilac-grey colour, which dissolves in water, giving a yellowish-green solution. The salt is insoluble in acetic acid. The violet acetate is obtained in a solid state, by leaving a solution of the normal acetate to evaporate to dryness under a bell-jar over strong sulphuric acid and in presence of acetic acid. The salt appears in the form of thin, brilliant, violet plates. When exposed to the air, the substance slowly loses acetic acid.

Mixed Argento-cupric Basic Salts.—Paul Sabatier.—By direct contact of cupric hydrate with silver solutions, the author obtained mixed basic salts, which may be divided into two distinct classes.—(1) Tricupric, of which he obtained the nitrate and the sulphate; and (2) Bicupric, of which he obtained the nitrate, chlorate, and hyposulphate. Except in the case of the sulphate, where the very slight solubility of the silver salt hinders the reaction, these salts can be equally well obtained, under certain conditions, by the action of silver oxide on the cupric salts.

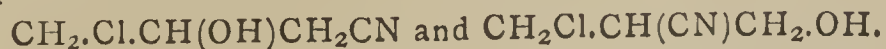
Purification of Iridium.—E. Leidie.—Instead of using the old dry method for the purification of iridium, the author suggests a method founded on the conversion of the metal into chloride and then treatment with sodium nitrite. The iron and lead are first precipitated as oxides, the gold in the form of the metal itself. There remains then double nitrites of ruthenium, rhodium, and iridium, and sodium osmate. The ruthenium and osmium can be eliminated as volatile peroxides, whilst the rhodium and iridium are converted into the double chlorides with sodium chloride, in which compound the two metals are easily separated. The author proposes to generalise this method to the purification of all the metals of the platinum group.

A Double Nitrite of Ruthenium and Potassium.—L. Brizard.—The author has obtained a new double nitrite of ruthenium and potassium, differing from the two already known in properties and constitution. Analysis shows the formula to be $\text{Ru}_2\text{H}_2(\text{NO}_2)_4 \cdot 3\text{NO}_2\text{K} \cdot 4\text{H}_2\text{O}$. The action of hydrochloric acid on this salt transforms it into the complex double chloride, which was the starting-point for the original preparation of the nitrite. The reaction, very slow in the cold, but becoming more rapid on boiling, may be represented by the equation—



Some Opium Alkaloids.—Emile Leroy.—The author has determined the heats of combustion, hydration, formation, solution, and neutralisation, for the following opium alkaloids:—Codeine, morphine, thebaine, papaverine, and narcotine.

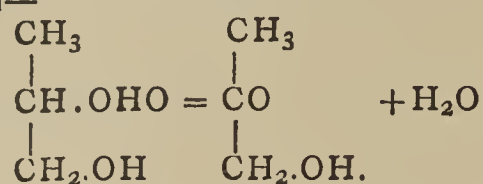
Dichlor-3,4-Butanoic Acid.—R. Lespieau.—The two possible formulæ for this acid are:—



The author's experiments show the former to be the most probable formula.

Oxidation of Propylglycol by Bromine Water.—André Kling.—When a mixture of 1 molecule of propylglycol with 2 molecules of bromine dissolved in water are exposed to the rays of the sun, the mixture after a time

becomes decolourised, and it is found that the propylglycol is transformed partially into acetol according to the equation—



Action of Bromine on Isobutyl Bromide in the presence of Anhydrous Aluminium Bromide and Aluminium Chloride.—A. Mouneyrat. — The author starts his series of experiments with monobromobutane, $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{Br}$. This is acted upon by bromine in the presence of aluminium bromide. Four substances are obtained from this reaction:— (1) Isobutylene bromide; (2) A tribromoisobutane, boiling at 130° (pressure 26 m.m.); (3) Tetrabromisobutane; (4) A tribromoisobutane, boiling at 112° , and with the probable formula $\text{CH}_3.\text{CBr}(\text{CH}_3)\text{CHBr}_2$. This latter is obtained in considerable excess of the others.

MISCELLANEOUS.

The Chemical Laboratory at Wiesbaden.—During the Summer Term, 1899, the Laboratory was attended by forty-eight Students. Of these, thirty-one were from Germany, three from Russia, two from England, two from Austria, and two from Holland, one from Switzerland, one from Belgium, one from France, one from Italy, one from Spain, one from Norway, one from Sweden, and one from the United States of America. There were three Assistants in the Instruction-Laboratory, and twenty-one in the Versuchsstationen (private laboratories). In the certified body of Teachers there has been no change. To this body belong the Directors, Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, Prof. Dr. E. Hintz, and also Dr. med. G. Frank, Dr. W. Lenz, Dr. L. Grünhut, and J. Huber (architect). The next Winter Term begins on October 16th. During the Summer Term, 1890, besides the scientific researches, a great number of analyses were undertaken in the different departments of the Laboratory (Versuchsstationen) on behalf of manufacture, trade, mining, agriculture, and hygiene.

INSTRUCTION IN

PURE CULTIVATION OF YEAST, According to Hansen's Methods.

Courses for Beginners, as well as for Advanced Students, in Physiology and Technology of Fermentations. Biological Analysis of Yeast. The Laboratory possesses a numerous collection of yeasts (brewers', distillers', wine, disease yeasts), moulds, and bacteria.

Manuals: E. Chr. Hansen, "Practical Studies in Fermentation," London (Spon), 1896. Alfred Jörgensen, "Micro-Organisms and Fermentation," London (F. W. Lyon), 1893.

The Laboratory supplies for direct use: Cultures of yeast for breweries, distilleries, wine manufactories, &c.

Further particulars on application to the Director—

ALFRED JÖRGENSEN, The Laboratory, Copenhagen, V.

CENTRAL TECHNICAL SCHOOLS FOR CORNWALL AT TRURO.

The Committee is prepared to receive Applications from gentlemen qualified to fill the position of PRINCIPAL.

Applicants must be qualified to teach the subjects enumerated in the Directory of the Science and Art Department as SCIENCE SUBJECTS, or be able to supervise the work of the other teachers in those subjects. The ART MASTER is a ready appointed. Favourable consideration will be given to those applicants who possess special qualifications in Organic and Agricultural Chemistry, and the gentleman appointed must be qualified to make analyses under the Food and Drugs Act. Applications will be received to the 7th September inclusive. Duties to commence at the end of September. Applicants to state what salary they require. No residence provided.

ALFRED BLENKINSOP,

Truro, Cornwall,
August 18th, 1899.

Secretary.

UNIVERSITY COLLEGE, BRISTOL. CHEMICAL DEPARTMENT.

Professor—SYDNEY YOUNG, D.Sc., F.R.S.

Lecturer—FRANCIS E. FRANCIS, B.Sc., Ph.D.

Demonstrator—D. H. JACKSON, M.A., B.Sc., Ph.D.

The SESSION 1899-1900 begins on October 3rd. Lectures on Inorganic, Organic, and Advanced Chemistry will be delivered during the Session. The Laboratories are fitted with the most recent improvements for the study of Practical Chemistry in all its branches. In the Evening the Laboratory is opened and Lectures on Inorganic Chemistry, at reduced fees, are delivered. Several Scholarships are tenable at the College.

CALENDAR, containing full information, price 1s. (by post 1s. 4d.).

For Prospectus and further particulars apply to—

JAMES RAFTER, Secretary.

THE DURHAM COLLEGE OF SCIENCE, NEWCASTLE-ON-TYNE.

EXAMINATION FOR JOHNSTON CHEMICAL
SCHOLARSHIP AND PRIZE.

The EXAMINATION for the award of this SCHOLARSHIP (value £60, tenable for one year), together with a PRIZE in books (value £5), will be held in September, 1899.

Candidates must send in their names ON OR BEFORE SEPTEMBER 23RD to the Secretary, from whom full particulars may be obtained.

REDRUTH SCHOOL OF MINES, CORNWALL.

Principal and Instructor in Inorganic Chemistry, Assaying, and Mineralogy	Mr. J. PAUL DE CASTRO, B.A. (Cantab.), F.C.S.
Mining, Ore Dressing, and Geology	Mr. THOMAS COLLINS.
Panning, Vanning, Rock Drilling, and Timber Cutting	Capt. W. HAMBLY (late H.M. Inspector in S. Africa).
Mine and Land Surveying	Capt. F. WICKETT (Bassett Mines, Ltd.).
Steam, Machine Construction, and Applied Mechanics	Mr. J. C. KEAST.
Mathematics	Mr. F. R. PASCOE, B.A. (Lond.) Mr. H. E. RUSSELL, B.A. (Dublin).

Instruction in Underground Work is to be obtained at the neighbouring mines.

For Prospectus apply to the Secretary—

W. K. WILTON.

CHEMICAL LABORATORY, WIESBADEN, GERMANY.

(Academical Institution of Instruction, supported by the State, with the right of developing Provision and Food Analysts for the final examination).

Directors. { Prof. H. FRESENIUS, Ph.D.
Prof. W. FRESENIUS, Ph.D.
Prof. H. HINTZ, Ph.D.

Practical Instruction in the Laboratory { Prof. H. FRESENIUS, Ph.D.
Prof. W. FRESENIUS, Ph.D.
Prof. E. HINTZ, Ph.D.

LECTURES.

Experimental Chemistry (Inorganic)	Prof. H. FRESENIUS, Ph.D.
Experimental Physics	Prof. W. FRESENIUS, Ph.D.
Stoichiometry	Prof. W. FRESENIUS, Ph.D.
Organic Chemistry	L. GRÜNHUT, Ph.D.
Chemical Technology	W. LENZ, Ph.D.
Microscopy, with exercises in Microscopic work	Prof. H. FRESENIUS, Ph.D. Prof. W. FRESENIUS, Ph.D. and Prof. E. HINTZ, Ph.D.
Chemistry and Analysis of Foods	Dr. med. G. FRANK.
Hygiene	J. HUBER.
Practical exercises in Bacteriology	
Technical Drawing, with exercises	

The next Session commences on the 16th of October. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. KREIDEL'S Verlag, at Wiesbaden, or to one of the Directors,

THE CHEMICAL NEWS.

VOL. LXXX., No. 2075.

(STUDENTS' NUMBER).

ADDRESS TO STUDENTS.

It cannot be denied that as the years roll on competition is getting more and more keen, and the choice of a profession requires more serious thought on the part of the student. On the other hand, it must be admitted that never before were there so many Colleges, Technical Schools, and Institutes for practically all classes of society to choose from, and where every student, no matter what his position, may be certain of obtaining the best instruction. It remains for him to take advantage of his opportunity.

We are afraid it is all too common for the first few months, and sometimes even half the year, to be practically wasted, followed by hurried reading and cramming. This may be all very well for getting through the examination, but it does not leave much good behind it: we therefore earnestly advise all young men now entering on their life-work, to work steadily and continuously throughout the year; they will then retain what they learn and lay a firm foundation for the more serious work which comes after College life.

We by no means advocate sticking too closely to books—"all work and no play makes Jack a dull boy;" a certain amount of exercise and athletics is as essential to keep the body in good health as is our daily food, and it not unfrequently occurs that the old Latin proverb—"Mens sana in corpore sano"—is verified, by the man who is best in the cricket field and in the boat also coming out very near the top in the examinations.

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

CANDIDATES for any Degree in this University must have passed the Matriculation Examination. No exemption from this rule is allowed on account of Degrees obtained or Examinations passed at any other University. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, and Medals depending upon them, are open to Women upon exactly the same conditions as to Men.

There are two Examinations for Matriculation in each year; one commencing on the second Monday in January, and the other on the second Monday in June.

The Examination is conducted by means of Printed Papers; but the Examiners are not precluded from putting, for the purpose of ascertaining the competence of the candidates to pass, *viva voce* questions to any candidate in the subjects in which they are appointed to examine. These Examinations may be held not only at the University of London, but also, under special arrangement, in other parts of the United Kingdom, or in the Colonies.

Every candidate for the Matriculation Examination must, not less than five weeks before the commencement of the Examination, apply to the Registrar for a Form of Entry, which must be returned not less than four weeks before the commencement of the Examination, accompanied by

a Certificate showing that the candidate has completed his sixteenth year, and by his Fee for the Examination. As no candidate can be admitted after the List is closed, any candidate who may not have received a Form of Entry within a week after applying for it must communicate immediately with the Registrar, stating the exact date of his application and the place where it was posted.

Every candidate entering for the Matriculation Examination for the first time must pay a Fee of £2 to the Registrar. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him, but he shall be allowed to enter for any subsequent Matriculation Examination upon payment, at every such entry, of an additional Fee of £1, provided that he comply with the Regulations in the preceding paragraph.

Candidates are not approved by the Examiners unless they have shown a competent knowledge in each of the following subjects:—Latin. Any one of the following Languages:—Greek, French, German, Sanskrit, or Arabic. The English Language, and English History, with the Geography relating thereto. Mathematics. Mechanics. One of the following branches of Science:—Chemistry, Sound, Heat and Light, Magnetism and Electricity, Botany.

The Examination in Chemistry is—Chemistry of the Non-metallic Elements; including their compounds, their chief physical and chemical characters, their preparation, and their characteristic tests.

A Pass Certificate, signed by the Registrar, will be delivered to each successful candidate after the Report of the Examiners has been approved by the Senate.

The first six candidates in the Honours Division of not more than twenty years of age at the commencement of the Examination will respectively receive an Exhibition or a Prize as follows:—The first of such candidates will receive an Exhibition of thirty pounds per annum for the next two years; the second among such candidates will receive an Exhibition of twenty pounds per annum for the next two years; and the third will receive an Exhibition of fifteen pounds per annum for the next two years; such exhibitions are payable in quarterly instalments provided that on receiving each instalment the Exhibitioner declares his intention of presenting himself either at the two Examinations for B.A., or at the two Examinations for B.Sc., or at the Intermediate Examination in Laws, or at the Preliminary Scientific M.B. Examination, and Intermediate Examination in Medicine, within three academical years from the time of his passing the Matriculation Examination.

Under the same circumstances, the fourth among such Candidates will receive a prize to the value of ten pounds in books, philosophical instruments, or money; and the fifth and sixth will each receive a prize to the value of five pounds in books, philosophical instruments, or money.

Any candidate who may obtain a place in the Honours Division at the Matriculation Examination in January is admissible to the Intermediate Examination either in Arts or in Science in the following July.

INTERMEDIATE EXAMINATION IN SCIENCE.

The Intermediate Examination in Science will commence on the second Monday in July.

No candidate (with the exception of such as have obtained Honours at the Matriculation Examination in the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. In addition, they will be examined practically in Simple Qualitative Analysis. This Examination will consist of six hours' examination by two printed papers and of six hours' practical work.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.Sc. EXAMINATION.

The B.Sc. Examination will be held on the fourth Monday in October.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously.

The Fee for this Examination is £5.

Examination for Honours.

For the examination for Honours in Chemistry two papers will be set and a two days' practical examination.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

DOCTOR OF SCIENCE.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

Every candidate for this Degree must state in writing the special subject within the purview of the Faculty of Science, as set out in the Programme of the B.Sc. Examination, upon a knowledge of which he rests his qualification for the Doctorate; and with the Form of Entry he shall transmit an original Dissertation or Thesis (at least six copies), printed, type-written, or published in his own name, treating scientifically some special portion of the subject so stated, embodying the result of independent research, or showing evidence of his own work, whether conducted independently or under advice, and whether based on the discovery of new facts observed by himself, or of new relations of facts observed by others, or, generally, tending to the advancement of Science. Every candidate may further specify any printed contribution or contributions to the advancement of Science which he has at any time previously published. If the Dissertation or Thesis be approved by the Examiners, the candidate shall be required to present himself at the University upon such day or days within the first twenty-one days of June as may be notified to him, and shall, at the discretion of the Examiners, be further tested, either orally or practically, or by printed questions or by all of these methods, with reference both to the special subject selected by him and to the Thesis.

PRELIMINARY SCIENTIFIC (M.B.) EXAMINATION.

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the second Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

No candidate shall be admitted to this Examination unless he shall have passed the Matriculation Examination. Not less than five weeks before the commencement of the Examination he must apply to the Registrar for a Form of Entry, which must be returned not less than four weeks before the Examination, accompanied with the candidate's fee.

The Fee for this examination is Five Pounds.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry—W. Odling, M.A., F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years. Students of Chemistry can obtain the degree of B.A. by passing preliminary examinations in Arts and in Science, and a final Honour examination in Chemistry. Chemistry may also be taken as part of the examination for a Pass degree. Graduates of other Universities suitably

qualified can obtain the degree of Bachelor of Science after an approved course of study or research and two years' residence.

University Laboratory.—Demonstrators, W. W. Fisher, V. H. Velej, F.R.S., J. E. Marsh.—The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

Christ Church Laboratory.—A. Vernon Harcourt, F.R.S. Scholarships of about the value of £80 are obtainable at the majority of the colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the Examination Statutes; the Student's Handbook to the University; and from the professors and college tutors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry—G. D. Liveing, M.A., F.R.S.

Jacksonian Professor of Natural and Experimental Philosophy—J. Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in the first or third term of residence or before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science in King's, Trinity, St. John's, St. Peter's, Clare, Trinity Hall, Queen's, Jesus, Christ's, Sidney, Pembroke, Caius, and Downing Colleges; the dates of the examinations vary, but are always fully advertised.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instructions. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, or from the *Cambridge University Calendar*.

UNIVERSITY OF DUBLIN.

TRINITY COLLEGE.

Professor of Chemistry—J. Emerson Reynolds, D.Sc., M.D., F.R.S.

Assistant Lecturer—Emil A. Werner, F.C.S., F.I.C.

Demonstrator—W. Haughton, M.B.

The general Laboratories include working accommodation for 120 Students, and the Quantitative and Research Laboratories for about 40 Students. The Laboratories will open on the 2nd of October. Lectures will commence about November 1st.

The Laboratories and the Lectures of the Professor of Chemistry can now be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The following Lectures are delivered:—

1. *Inorganic Chemistry and Chemical Philosophy*.—Elementary, first year; advanced, second year.
2. *Organic Chemistry*.—General, second year; advanced, third year.
3. *Metallurgy*.—A Course for Engineering and Technical Students.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The Summer Course of Practical Chemistry for Medical Students begins during the first week in April and terminates with the first week in July.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

KING'S COLLEGE.

(DIVISION OF ENGINEERING, ARCHITECTURE, AND APPLIED SCIENCE).

Professor of Chemistry—J. M. Thomson, F.R.S., F.C.S.

Demonstrator of Practical Chemistry—Herbert Jackson, F.C.S.

Assistant Demonstrator—P. H. Kirkaldy, F.C.S.

The Academical Year consists of Three terms. The days fixed for the Admission of New Students in the Academical Year 1899-1900 are October 3, January 17, and April 25.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a view of the conditions suitable for the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic Elements and their principal compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated. Examinations of the Class, both *vivâ voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, and they go through a course of Manipulation in the most important operations of Chemistry, including the first steps of Analysis. Any Student of this Division may be admitted to this Class at any period of his study on payment of an extra fee.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday, on which day the hours are from ten till one.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Special hours and fees are arranged for the convenience of such Third Year Students as wish to study Analytical Chemistry.

Fees.—Chemistry per term, £3 3s.; per ann., £8 8s.; Practical Chemistry per term, £4 4s.; per ann., £10 10s.; Experimental and Analytical Chemistry—Five days a week: One month, £4 4s.; Three months, £10 10s.; Six months, £18 18s.; Nine months, £26 5s. Three days a week: One month, £2 12s. 6d.; Three mos., £6 6s.; Six mos., £11 11s.; Nine mos., £15 15s.

METALLURGY.

Professor—A. K. Huntington, F.I.C., F.C.S., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is paid to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open

during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery.

PHOTOGRAPHY.

Lecturer—Prof. J. M. Thomson, F.R.S., F.C.S.

In addition to the regular College Course in Photography occasional classes may be formed. For further particulars application should be made to Prof. Thomson.

EVENING CLASSES.

Classes for Evening Instruction in various subjects are held during the Winter Session.

UNIVERSITY COLLEGE.

FACULTY OF SCIENCE.

Professor—William Ramsay, LL.D., F.R.S., &c.

Assistants—Morris Travers, D.Sc., Alexander Kellas, B.Sc., and E. C. C. Baly, F.I.C.

The Session is divided into three Terms, as follows, all the dates being inclusive:—

First Term, from Tuesday, October 3rd, until Friday, December 22nd;

Second Term, from Tuesday, January 16th, 1900, till Friday, March 30th;

Third Term, from Tuesday, April 24th, till Friday, June 29th. Class Examinations begin on June 13th.

Junior Courses of Inorganic Chemistry.

First Term: Tuesday, Thursday, and Saturday at 10., Latter half of Second and Third Term: Tuesday, Thursday, and Saturday. Fee:—£4 4s.

These Courses will each consist of about thirty lessons, partly theoretical and partly practical, on the non-metallic elements. Frequent exercises will be given.

Senior Course of Inorganic Chemistry.

First and Second Terms: The Class meets four times a week, on Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

Fees:—For the Course, £7 7s.; Perpetual, £9 9s.; for the First or Second Terms, £4 4s.

This Course and the Practical Class cover the subject as prescribed for the Preliminary Scientific (M.B.) and Int. Examination in Science of the University of London.

For the Preliminary Scientific Examination Students who take the three subjects for that examination in July attend during the First and Second Terms.

Advanced Course of Chemistry.

Second and Third Terms.—The class meets twice a week, on Tuesdays and Thursdays, at 9, beginning on January 9. The hour will be altered by special arrangement with the class if necessary.

Fee:—For the Course, £3 3s.; for a Term, £2 2s.

This Course will be found suitable for those about to proceed to graduation as Bachelor of Science in London University, and to those who intend to choose Chemistry as a profession. Such students should also work in the Laboratory during as many hours as they can spare.

Organic Chemistry.

Tuesday, Thursday, and Saturday, at 9, in the First Term; Tuesday, Thursday, and Saturday, at 10, in the Second Term; and Tuesday and Thursday at 9, and Saturday at 11, in the Third Term. The hour of meeting will be altered should the class desire it.

This Course of Organic Chemistry is intended for those who are studying the subject from a scientific standpoint. Candidates for Honours at the Int.M.B. are, however, recommended to attend this Course besides the Special Summer Course.

The Course includes the subjects required at the B.Sc. Examination, Pass and Honours; but no previous acquaintance with Organic Chemistry will be expected of those joining the Class.

Fee:—For the Course, £6 6s.; for the Second and Third Terms, £4 14s. 6d.; for a Term, £2 12s. 6d.; for a Second Course, £3 3s.

Practical Classes.

Practical Classes in Inorganic and Organic Chemistry are conducted by the Assistants.

Analytical and Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

The Laboratory Course includes the Practical Chemistry required at the following Examinations of the University of London:—Prel. Sci. (M.B.), Intermediate M.B., Intermediate Science, B.Sc.

Students who wish to attend the Lectures on Chemical Technology may acquire here the requisite knowledge of Practical Chemistry and Analysis.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Course qualifies Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. The Tuffnell Scholarship (£100 for two years) will also be competed for in the Session 1899-1900; also the Cloth-worker's Scholarship of £30.

ROYAL COLLEGE OF SCIENCE AND ROYAL SCHOOL OF MINES.

Professor—W. A. Tilden, D.Sc., F.R.S.

Assistant Professor—W. P. Wynne, D.Sc., F.R.S.

Demonstrators—H. Chapman Jones and M. O. Forster, Ph.D.

Assistants—G. S. Newth, G. T. Morgan, B.Sc., and J. A. Craw.

The Royal College of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Science and Art Department. The Royal School of Mines is incorporated with the Royal College of Science. Students entering for the Associateship of the Royal School of Mines obtain their general scientific training in the Royal College of Science. The instruction in the Royal College of Science is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Royal College of Science, or of the Royal School of Mines. Students who are not candidates for the Associateship are permitted to enter as occasional students in one or more special branches of science, and on passing the examination receive a Certificate to that effect. The Associateship of the Royal College of Science is given in one or more of the following divisions:—Mechanics, Physics, Chemistry, Biology, and Geology, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction, which lasts for three years, is the same for all the divisions during the first year, after which it is specialised in accordance with the Scheme detailed in the Prospectus of the School.

The Session is divided into two Terms. The first Term begins on the 5th of October and ends about the middle of February. The second Term begins in the middle of February and ends about the middle of June.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third year, the successful candidates being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first year, and, in the second and third year, those subjects prescribed as necessary for the division in which he seeks to obtain his Associateship. A student who goes through the prescribed course of instruction in any subject and passes the necessary examinations receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table:—

	Lectures.	Laboratory.
	£	£
Chemistry	3	13
Physics	5	12
Biology with Botany	5	12
Geology with Mineralogy ..	4	8
Mechanics	4	6
Metallurgy	2	13
Mining	4	
Astronomical Physics	2	3

Mathematics and Mechanical Drawing, £3 per term. Model and Freehand Drawing, £1 per term. Descriptive Geometry, £3 per session. Mine Surveying, £10.

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to about £40.

Both the private and the State-aided students are required to furnish themselves with certain instruments and apparatus before the commencement of the courses. These are enumerated in the syllabuses of the several subjects.

Officers of the Army, Navy, and Civil Service, recommended by their respective Departments, are admitted to the Lectures and Laboratories at half fees.

Associates of the Royal College of Science or of the Royal School of Mines have the privilege of free admission to the Library and to all the courses of lectures.

Bona fide teachers qualified to earn payments for teaching Science according to the rule of the Science and Art Directory may obtain permission to attend free any course of lectures.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

Summer Courses for Teachers.—Short courses of instruction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 250 teachers are admitted to them, and they receive third class railway fare to and from South Kensington, and a sum not exceeding £3 towards their expenses. (See Science and Art Directory).

Working Men's Lectures.—Notification of these will be given in the newspapers.

THE SCHOOL OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Fifty-eighth Session will commence on Monday, October 2nd, 1899.

Professors—Chemistry, J. Norman Collie, Ph.D., F.R.S. (Dean); Botany, J. Reynolds Green, Sc.D., F.R.S., F.L.S.; Materia Medica and Pharmacy, Henry G. Greenish, F.I.C., F.L.S.

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the

end of March. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies.

Prospectuses and further information may be obtained from Mr. Richard Bremridge, Secretary and Registrar, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES,
ABERYSTWYTH.
UNIVERSITY OF WALES.

Professor—H. Ll. Snape, D.Sc. (Lond.), Ph.D. (Göttingen), F.I.C.

Demonstrators—H. Hibbert, B.Sc. (Vic.), and A. Brooke, Ph.D. (Strassburg).

Lecturer in Agricultural Chemistry—J. Alan Murray, B.Sc. (Edin.).

The College is open to male and female students above the age of sixteen years. The Session commences on Tuesday, October 3, on which day all Students will be expected to meet the Professors in the Examination Hall of the College.

Lecture Courses.—(1) Matriculation Course; three lectures weekly during the Michaelmas and two weekly during the Lent and Easter Terms. (2) Intermediate Science Course; four lectures weekly during the Lent and Easter Terms. (3 and 4) B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, two lectures weekly on Chemical Theory. (Courses A and B will generally be given in alternate Sessions; for 1899-1900, Course A). (5 and 6) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly throughout the Session.

Laboratory Courses.—The Laboratory is open daily from 10 a.m. to 1 p.m., and from 2.15 to 5 p.m., except on Wednesdays and Saturdays. Classes for the Systematic Study of Qualitative and Quantitative Analysis will be formed, and Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the University of Edinburgh and the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 12s. 6d. per term, and for twelve hours, 25s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10

to £40 per annum will be offered for competition at examinations which commence on September 19, and exhibitions are awarded at the end of the Session on the results of the class examinations.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Prospectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES,
BANGOR.

A CONSTITUENT COLLEGE OF THE UNIVERSITY OF WALES.

Chemistry.—Professor, James J. Dobbie, M.A., D.Sc. Demonstrator, Alexander Lauder, F.C.S. Assistant Lecturer in Agricultural Chemistry, F. V. Dutton.

Physics.—Professor, Andrew Gray, M.A., LL.D., F.R.S.

The Session opens October 3rd, 1899. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Matriculation Course.—Subjects: Those prescribed for the Matriculation Examination of the University of Wales. Fee for the Session £3 3s.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Session, £3 13s. 6d.

B.Sc. Course.—Advanced Inorganic Chemistry. Fee for the Session, £3 3s.

Agricultural Chemistry.—Fee, £2 2s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 4 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s.; twenty-four hours, £4 4s. Composition Fee for all Laboratory Classes of the Intermediate Science Course taken in one year, £4 4s.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and students can make one *Annus medicus* at the college. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES
AND MONMOUTHSHIRE, CARDIFF.

Professor—C. M. Thompson, M.A., D.Sc., F.C.S.

Demonstrators—E. P. Perman, D.Sc., F.C.S., and A. A. Read, F.I.C., F.C.S.

The Session commences October 2nd, and terminates on June 22nd, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 50 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London. Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of about 80 lectures held during the Lent and Summer terms in continuation of the Junior Course, and is the qualifying course for the Intermediate Examination of the University of Wales. Together with laboratory practice, it will cover the subjects required for the Intermediate Examination in Science and the Prel. Sci. (M.B.) Examination of the University of London. Fee, £4 4s.

The Senior Course consists of some 90 lectures on Organic Chemistry; Fee, £3 3s.

A course of 20 lectures on Qualitative Analysis and a short course on Organic Chemistry will also be given.

The following lectures on Metallurgy will be given by Mr. Read:—10 lectures on Fuel; Fee, 10s. 6d. 20 lectures on General Metallurgy; Fee, £1 1s. 30 lectures on the Manufacture of Iron and Steel; Fee, £1 1s. A practical course on Iron and Steel Analysis will also be held,

and practical instruction in Dry Assaying will be given in the Metallurgical Laboratory, which is fitted with the necessary furnaces and apparatus.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £3 3s. per session; twelve hours, £2 2s. per term; eighteen hours, £3 3s. per term; twenty-four hours £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students wishing to graduate at a Scottish University, or preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of Wales and of the University of London may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY COLLEGE, BRISTOL.

Professor of Chemistry—Sydney Young, D.Sc., F.R.S.

Lecturer—Francis E. Francis, B.Sc., Ph.D.

Demonstrator—D. H. Jackson, M.A., B.Sc., Ph.D.

The session 1899-1900 will begin on October 3. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratories. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articulated pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the College. Several Scholarships are tenable at the College. Full information may be obtained from the Secretary.

DAY LECTURES.

Inorganic Chemistry.

The Courses treat of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Junior Course.—Two Lectures a week will be given during the First and Second Terms. Fee, £3 3s.

General Elementary Science (London Matriculation).—

A course of about 16 Lectures will be delivered in the Third Term. Fee, including Physics (1st and 2nd Terms), £5 5s.

Special Course.—A special course of Lectures is also given to Engineering Students.

Intermediate Course.—Three Lectures a week will be given throughout the Session. Fee, £5 5s. There will be tutorial classes in connection with the Junior and Senior Courses.

Advanced Course (Parts I. and II.).—One Lecture a week in each part will be given throughout the Session. Fee for each course, £2 12s. 6d.

Organic Chemistry.

This Course will relate to the more important groups of the Compounds of Carbon.

Two Lectures a week will be given throughout the Session. Fee, £3 3s. An advanced course of lectures will also be given one day a week during the session. Fee, £2 12s. 6d.

Practical Chemistry.—Laboratory Instruction.

The Laboratory will be open daily from 10 a.m. to 5 p.m., except on Saturdays, when it will be closed. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, and Inorganic and Organic Research. Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures. Fees in Guineas—

	5 Days a Week.	4 Days a Week.	3 Days a Week.	2 Days a Week.	1 Day a Week.
Per Session	15	12½	10	7½	5
„ Two Terms ..	11	9	7½	5½	3½
„ One Term ..	7	6	4½	3½	2½

Students may arrange to divide their days of laboratory work into half-days.

Chemical Scholarship.—Among others, a Chemical Scholarship of £25 is offered for competition.

EVENING LECTURES.

Two courses of Lectures will be delivered during the First and Second Terms; they will be devoted to the consideration of the general Principles of Chemistry and Chemical Physics and the Chemistry of Non-Metallic and Metallic Elements. Special attention will be paid throughout to those products which have a practical application in the Arts and Manufactures. Fee for each course, 7s. 6d.

General Elementary Science.—A course of Lectures, primarily intended for Candidates for Matriculation, will be given during the First Term. Fee (including Physics), 7s. 6d.

Practical Chemistry—Laboratory Instruction.—The Laboratory will be open two evenings a week from 7 till 9. Instruction will be given in Qualitative and Quantitative Analysis, and in the Preparation of Chemical Products. Fees:—(Two Terms) Two Evenings, 25s.; One Evening, 15s. (One Term) Two Evenings, 15s.; One Evening, 10s. 6d.

University College, Bristol, has been approved by the Council of the Institute of Chemistry as a College at which all the subjects required for the admission of Associates to the Institute are taught.

The Calendar of the College, price 1s. (post-free, 1s. 4d.), containing detailed information of the various Courses, may be obtained on application to the Secretary.

MASON UNIVERSITY COLLEGE, BIRMINGHAM.

Professor—Percy F. Frankland, Ph.D., B.Sc., F.R.S.

Assistant Lecturer—C. F. Baker, Ph.D., B.Sc.

Demonstrator—W. R. Innes, Ph.D.; M.Sc.

Lecturer on Metallurgy—Godfrey Melland, F.I.C.

The Session will be opened on October 3rd, 1899.

Elementary Course.

Forty Lectures adapted to the requirements of beginners

will be given in the Winter and Spring Terms. Lecture days—Wednesdays and Fridays at 11.30.

Persons entirely unacquainted with Chemistry are recommended to attend this Course before entering for the General Course. Candidates for the Matriculation Examination of the University of London also are advised to attend this Course.

General Course.

The General Course of Lectures on Chemistry will be found useful by Students who are afterwards to become Engineers, Architects, Builders, Brewers, or Manufacturers (such as Metallurgists, Alkali, Soap, Manure, Glass, or Cement Makers, Bleachers and Dyers, &c.)

Students preparing for the Intermediate Examination in Science and Preliminary Scientific (M.B.) Examination of the University of London should attend the Lectures on Inorganic Chemistry (Winter and Spring Terms) and the Organic Lectures (Summer Term).

Candidates for Intermediate Examinations in Medicine will in general require only that part of the course (Summer Term) which relates to Organic Chemistry.

The full course, extending over three terms, will also satisfy the requirements of Students preparing for the Associateship of the Institute of Chemistry, so far as attendance at lectures on General and Theoretical Chemistry is concerned.

1. From October to March (Winter and Spring Terms). About eighty lectures on Inorganic Chemistry and Chemical Philosophy will be given on Mondays, Tuesdays, Wednesdays, and Thursdays from October to December, and on Mondays, Tuesdays, and Wednesdays from January to March, at 9.30 a.m. A Tutorial Class is held in connection with this Course once a week throughout the Session. Fee, £5 5s. for the course.

2. April to June (Summer Term). About thirty lectures will be given on Elementary Organic Chemistry, or the chemistry of the most important series of carbon compounds. This course will include all the subjects required for the Intermediate Examination in Medicine of the University of London. Lecture Days—Monday, Wednesday, and Friday at 9.30. Fee, £1 11s. 6d.

The General Course (including Inorganic and Organic lectures) qualifies for graduation in the medical faculties of the universities of Edinburgh, Glasgow, Aberdeen, and Durham.

Special Courses of Lectures and of Laboratory Instruction are given for Medical Students preparing for the Conjoint Board Examinations.

Advanced Course.

An Advanced Course for the study of Theoretical Chemistry and those parts of the subject which are required for the degree of B.Sc. in the University of London will meet twice a week. Fee for the session, £3 3s.

Laboratory Practice.

The College Laboratory is open daily from 9.30 to 5, except on Saturdays, when it is closed at 1 p.m.

Candidates for Intermediate Examination in Science, Preliminary Scientific (M.B.), B.Sc., and Intermediate Examination in Medicine of the University of London, may obtain in the Laboratory of the College the instruction necessary. The three months Course of Practical Chemistry for the B.Sc., Edinburgh, in the department of Public Health, may be taken in the Mason College Laboratory. Fees:—

	All day.	Three hours per day.	Three hours per day; five days a week.	Three hours per day; five days a week.
	Guineas.	Guineas.	Guineas.	Guineas.
One Term ..	7	4½	4	2½
Two Terms .	13	8½	7½	5
Three Terms	18	12	11	6½

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Metallurgy.

Three Courses of Ten Lectures will be given on the Principles and Practice of Metallurgy. Fee, 10s. 6d. for each of the first two courses, and for each of the two sections of the third course. A more advanced course of about sixty lectures upon selected subjects is also given.

There is a separate laboratory for metallurgical students in which provision is made for instruction in assaying, &c.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of about £96 each are awarded annually in September.

Bowen Scholarship.—One Open Scholarship in Metallurgy of the value of about £96 is awarded annually in September.

Forster Research Scholarship.—A Scholarship of the value of £50 is annually awarded.

For particulars apply to the Registrar.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturers.

BRADFORD TECHNICAL COLLEGE.

CHEMISTRY AND DYEING DEPARTMENT.

Head Master—W. M. Gardner, F.C.S.

Demonstrator and Lecturer on Geology—Dr. W. F. Sutherst, Ph.D. (Geneva), *Chemiste-Diplômé de Zürich.*

Lecturer on Botany and Biology—William West, F.L.S.

Assistant—E. Gibson.

The College Session is divided into three terms. The Session commences on September 11th and terminates on July 21st. The course of instruction extends over three years, and embraces Lecture Courses on Inorganic and Organic Chemistry, the technology of the textile fibres, mordants, natural and artificial colouring matters, technical analysis, and laboratory practice in analytical chemistry, chemical preparations, and dyeing. Fee, £5 per Term, or £13 per Session.

During the first and second terms Evening Classes are held for the benefit of persons engaged during the day.

A General Course preparing for the Pharmaceutical Society's examinations has been arranged.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

CHEMICAL DEPARTMENT.

Professor—Prof. E. Kinch, F.C.S., F.I.C.

Assistant—W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation, of stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agriculture.

tural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

VICTORIA UNIVERSITY. THE YORKSHIRE COLLEGE, LEEDS.

Professor of Chemistry—Arthur Smithells, B.Sc. Lond., F.I.C.

Lecturer in Organic Chemistry—Julius B. Cohen, Ph.D., F.I.C.

Assistant Lecturer and Demonstrator—T. S. Patterson, Ph.D.

Demonstrators—J. McCrae, Ph.D., and H. M. Dawson, B.Sc.

The Session begins October, 1899.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m. Fee for the Course, £4 4s.

2. Inorganic Chemistry.—Honours Course, Metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.

3. Inorganic Chemistry.—Honours Course, Non-metals. Tuesday and Thursday at 9.30 a.m. Fee, £3 13s. 6d.

4. Organic Chemistry.—Tuesday, Thursday, and Saturday at 12 noon. Fee £3 13s. 6d.

5. Organic Chemistry Honours Course.—Wednesday and Friday at 12 noon. Fee, £2 12s. 6d.

6. Theoretical Chemistry.—Advanced Course. Tuesdays and Thursdays at 9.30 a.m. Fee, £2 12s. 6d.

7. Chemistry for Teachers.—Saturdays from 9.30 to 12.30 in the first and second terms. Fee, £4 4s.

Laboratory Courses.

The College Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—Students working six days per week, £21; five, £18 18s.; four, £16 16s.; three, £13 13s.

Class in Practical Chemistry, Saturday mornings, from 9.30 to 12.30. Fee £1 11s. 6d.

Practical Course in Sanitary Chemistry.—Tuesdays and Thursdays from 2 to 5 p.m., from January to March. Fee, £5 5s.

Dyeing Department.

Professor—J. J. Hummel, F.I.C.

Lecturer and Research Assistant—A. G. Perkin, F.R.S.E.

Assistant Lecturer—R. B. Brown.

This Course extends over a period of three years, and is intended for those who wish to obtain a full scientific and practical education in the art of dyeing. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, e.g., the sons of manufacturers, calico printers, managers, master dyers, &c.

Leather Industries Department.

Professor—H. R. Procter, F.I.C.

Assistant Lecturer and Demonstrator—Andrew Turnbull, Ph.D.

The full Courses, which extend over a period of either two or three years, are suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and are recommended to sons of tanners. The Courses include instruction in chemistry, a modern language, leather manufacture, and practical work in the Leather Industries Laboratory and Dye-house.

Agricultural Department.

Professor—J. R. Campbell, B.Sc.

Lecturer in Agricultural Chemistry—H. Ingle, F.I.C.

The full Course occupies two years, and includes instruction in chemistry, physics, mathematics, geology, botany, forestry, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out-door agriculture.

Research Students are admitted to the College Laboratories on reduced terms.

Several valuable Scholarships are at the disposal of the College, viz., the Salt, Akroyd, Brown, Emsley, Craven, Leeds City Council, and Clothworkers' Scholarships, and one of the 1851 Exhibition Scholarships. The West Riding County Council Scholarships are tenable at the Yorkshire College.

UNIVERSITY COLLEGE, LIVERPOOL.

Professor—J. Campbell Brown, D.Sc.

Lecturer on Organic Chemistry—C. A. Kohn, B.Sc., Ph.D.

Lecturer on Metallurgy—T. L. Bailey, Ph.D.

Demonstrators and Assistant Lecturers—T. L. Bailey, Ph.D., C. A. Kohn, B.Sc., Ph.D., and A. W. Titherley, M.Sc., Ph.D.

Assistant—H. H. Froyssell.

The Session commences October 2nd.

Entrance Scholarship Examination takes place early in May each year.

The William Gossage Chemical Laboratory has been completed and opened for Advanced Students, the Metallurgical Laboratory has been enlarged, and new Gas Analysis and Electro-Chemical rooms have been added, with a third Lecture Room.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in Victoria University; for Degrees in Medicine of Victoria, London, and Edinburgh; for the Pharmaceutical Diplomas; for a special Technological Certificate of University College; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry of Great Britain and Ireland, and other Examination Boards.

Lecture Courses.

General Elementary Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, including Practical class, £4.

Pharmacy Courses: Junior, £3; Senior, £3.

Dental Course, Lectures and Practical. Fee, £5 5s.

Course A.—Non-metals. Fee, £3.

Course B.—Metals. Fee, £3.

Course C.—Organic Chemistry. Fee, £3.

Course H.—Special Organic Subjects. Fee, £2.

Course D.—Physical Chemistry. Fee, £1.

Course E.—History of Chemistry and of the Development of Modern Chemical Philosophy. Three Terms. Fee, £2.

Courses F.—Applied Chemistry and Metallurgy: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) General Principles of Metallurgy. (3) Iron, Steel, and Aluminium. (4) Copper, Lead, Silver, and Gold, and other Metals. (5) Distillation of Coal and Tar Industries. (6) Fuel and Gas. (7) Chemistry Applied to Sanitation. (8) Technical Gas Analysis. (9) Electro-chemical work. Three terms. Fee, each course £1 10s.

Practical Classes.

(1) Junior. (2) Intermediate: Qualitative Analysis of Inorganic Substances and of some of the more common Organic Substances. (3) Revision Class. (4) Senior: Practical Organic. (5) Practical Exercises on Technology, Pharmaceutical Chemistry, Saitanry subjects, Examination of Water and Air, of Animal Secretions, Urinary Deposits, Calculi, and Poisons. (6) Quantitative Class.

Chemical Laboratory.

The Chemical Laboratories provide accommodation for every kind of chemical and metallurgical work.

The William Gossage Laboratory, opened in 1897, con-

sists of a large and well-fitted general Laboratory for advanced Students, a new gas analysis room, an additional lecture-room for Metallurgy and other classes, and an addition to the Research Laboratory. New stores for students' apparatus and chemicals have also been built and placed in charge of a skilled dealer.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study, for which a full curriculum is provided.

TABLE OF FEES.

Per Week.	One Term, Three Months.	Three Terms, One Session.
One day	£4	£7
Two days	5 10s.	10
Three days	7	13
Four days	9	16 10s.
Whole week	10 10s.	21

Pharmaceutical Course (see special syllabus).

Technological Curriculum.

Preliminary Year.—Chemistry, the Elementary Course. Practical Classes 1 and 2. Mathematics, or Mechanics, Elementary Engineering, Drawing, and Design (in this or one of the following years). German. Or, the Victoria Preliminary Course and Examination may be taken.

First Year.—Chemistry—Courses A and B; Chemical Laboratory three days per week; Technological Chemistry, Course F. Physics, with laboratory work, one day per week. Mathematics (intermediate). German. Engineering, First Year Course, Autumn and Lent Terms. Intermediate B.Sc. Examination may be passed.

Second Year.—Chemistry, Lecture Course C, on Organic Chemistry, Lecture Course E or D, Technological Chemistry, Course F. Chemical Laboratory, four days per week. Engineering, Mathematics, or Physics (Advanced). The Final Examination for the Victoria B.Sc., or the Intermediate Examination of the Institute of Chemistry, may be taken.

Third Year.—In the third year the student should begin to specialise. The following are possible alternatives:—1. Courses D and F; Course H. Any other Courses omitted in a previous year. Laboratory, five days per week. The Degree of B.Sc. in the Honours School of Chemistry may be taken. 2. Metallurgical Classes. Metallurgical Laboratory, two days per week. Chemical Laboratory, Gas Analysis, and Electro-chemistry, two days per week. Physical and Electrotechnical Laboratory, one day per week. 3. Courses D, E, and F. Physics (Senior Course). Chemical Laboratory, four days per week. Physical Laboratory, one day per week. 4. Courses D and F, and a course on Chemistry applied to manufacturing operations. Chemical Laboratory, three or four days per week. Engineering Laboratory and Electrotechnical Laboratory, one day per week. Students may finally choose a special subject either of research or of applied Chemistry. The Final Examination for the Associateship of the Institute of Chemistry of Great Britain and Ireland may be taken after 1, 2, or 3. Those who have taken the Ordinary Degree of B.Sc. may pass the Victoria M.Sc. Examination in any subsequent year.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, will be competed for on December 7, 8, and 9, 1899, on an Examination in subjects which are included in the first two and a half years of the above curriculum. Candidates should send in their names to the Principal not later than November 15. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

Evening Classes.

Classes, including laboratory work, will be held on Chemistry, Metallurgy, and on Organic Chemistry.

The Prospectus containing full particulars may be obtained from the Registrar, University College, Liverpool.

DURHAM COLLEGE OF SCIENCE,
NEWCASTLE-ON-TYNE.

Professor of Chemistry—P. Phillips Bedson, M.A., D.Sc., F.I.C., F.C.S.

Lecturer in Chemistry—Saville Shaw, M.Sc., F.C.S.

Lecturer in Agricultural Chemistry—S. Hoare Collins, F.I.C., F.C.S.

Assistant Lecturers and Demonstrators—F. C. Garrett, M.Sc., F.C.S., and J. A. Smythe, B.Sc., Ph.D.

The Session will commence on September 25th, 1899.

Lectures begin on October 3rd, 1899.

1. *General Course.*—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. A section of this Course will be devoted to an outline of Organic Chemistry. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 5th. Fee, £3 10s. for the Session.

Second Year Course.—The Lectures for the second year students consist of a course of Lectures on Inorganic Chemistry, extending from October to December, and a course of Lectures on Organic Chemistry from January to the end of the Session. The Class will meet on Tuesdays and Thursdays at 11 a.m., and Fridays at 3 p.m., and will commence on October 6th. Fee for Session, £3 10s.; for Inorganic alone £1 10s.; and for Organic alone £3.

Advanced Classes will be formed for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for the course, £3 10s.

A Lecture Course in Analytical Chemistry will be given on Mondays, at 3 p.m.

Metallurgy and Assaying.—Lecturer, Saville Shaw, M.Sc., F.C.S. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry Assaying, and in the preparation and analysis of Alloys, &c. Fees as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10s.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working two days, £2 10s. per term, £6 per session; one day per week, £1 10s. per term, £3 10s. per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subject professed in the College as will enable them to pass the Examinations for the title of Associate in Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in reading, writing from dictation, English or Latin Grammar, arithmetic (including decimals), and geography. Registered students in medicine are exempted from this examination, or stu-

dents who produce a certificate of having passed either of the two following examinations:—

1. Durham Examination for certificate of proficiency in General Education, held in March and September.

2. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

Associateship in Science.—Every candidate for the Associateship in Science will be required to satisfy the examiners in—Mathematics, Physics, Chemistry, and either Geology or Natural History—in an examination to be held at the end of the candidate's first year. Associates in Science are admissible one year after obtaining the title of Associate to examination for the degree of Bachelor of Science of the University of Durham.

Exhibitions.—Three Exhibitions of the value of £25, £15, and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Wednesday, September 28th.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Two Exhibitions of £15 each will be awarded at the next examination of "Persons not members of the University," which will be held at Durham in March next.

Several other valuable Scholarships are available for students, including the Johnston Chemical Scholarship of the value of £60 for one year.

OWENS COLLEGE, VICTORIA UNIVERSITY, MANCHESTER.

Professor and Director of the Chemical Laboratory—Harold B. Dixon, M.A., F.R.S.

Professor of Organic Chemistry—W. H. Perkin, Ph.D., F.R.S.

Demonstrators and Assistant Lecturers—George H. Bailey, D.Sc., Ph.D.; W. A. Bone, D.Sc.; P. J. Hartog, B.Sc.; E. J. Russell, B.Sc.; D. L. Chapman, B.A.; and H. C. H. Carpenter, B.A.

Demonstrator in Organic Chemistry—W. T. Lawrence, B.A., Ph.D.

Lecturer in Technical Organic Chemistry—Jocelyn F. Thorpe, Ph.D.

Assistant Lecturer in Metallurgy—Dr. Bone.

The Session begins on October 3, 1899, and ends on July 1, 1900.

The instruction is given by means of Experimental Lectures and Tutorial Classes. The Chemical Classes form part of the Courses for Chemistry in the University.

Chemistry Lecture Courses.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 9.30, during Lent Term.

These courses are intended for Medical Students and others beginning the study of chemistry.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30 a.m., during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Mondays, Wednesdays, Fridays, 3.30 p.m., during the two Winter Terms. The Metals.

Third Year Honours Course.—At times to be arranged. Physical Chemistry.

Organic Chemistry (General).—Mondays and Fridays, 9.30, during two Winter Terms.

Organic Chemistry (Advanced).—Tuesdays and Thursdays, 9.30, during the two Winter Terms.

History of Chemistry and Chemical Philosophy.—Wednesdays, 9.30, during the Session.

METALLURGY.—*Lectures:* The Metallurgy of Copper, Lead, Silver, Gold, and the Metallurgy of Iron and Steel will be given in alternate years. *Practical:* The Laboratory will be open to students every day.

The Chemical Laboratories are open daily from 9.30 a.m. to 4.30 p.m., except on Saturdays, when they are closed at 12.30 p.m.

Courses for B.Sc. Degree.—To qualify for the B.Sc. Degree of the Victoria University, Students have to attend a prescribed course of study extending over three years, and to pass the Preliminary Examination of the University either on entering or at the end of a year's Course.

The Honours Course of Chemistry is as follows:—
First year: First year Honours Lectures; Mathematics (3 hours a week); Physics (3 hours a week); a Language (3 hours a week); Chemical Laboratory (3 days per week).
Second year: Second year Honours Lectures; General Organic Lectures; Applied Chemistry Lectures; Physics Laboratory (1 day per week); Chemical Laboratory (3 days per week).
Third year: Third year Honours Lectures; Honours Organic Lectures; History of Chemistry Lectures; Chemical Laboratory (5 days per week).

The following awards are made to successful Students in the Honours Examination:—A University Scholarship of £50; a Mercer Scholarship of £25. A University Fellowship of £150 is awarded annually among the Graduates in Science for the encouragement of Research. Among the *College* Scholarships open to Chemical Students are the Dalton Chemical Scholarship, £50 per annum for two years; the 1851 Exhibition Scholarship; the Levinstein Exhibition; &c.

Applied Chemistry.

First Course.—Sulphuric Acid and Alkali Manufactures. General Principles of Chemical Engineering.

Second Course.—The Chemistry of Fuel. The Manufacture of Illuminating Gas and Gaseous Fuel.

Third Course.—Natural and Artificial Dye-stuffs, and the Principles of Dyeing and Printing.

Certificates in Applied Chemistry.

The course extends over a period of three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

Before admission to the first year's course students are required to give such evidence of elementary knowledge of Mathematics and Chemistry as shall be considered satisfactory by the Senate.

The first year's course is the same for all students working for the certificate.

In the second and third years a choice may be made between Inorganic and Organic Chemistry. By this division of the subject a student wishing to apply himself specially to the inorganic side of the science, may attend during his second year the Honours course in Metals, and courses on Geology or Mineralogy, and during his third year, courses on Metallurgy and on Geology or Mineralogy; while a student wishing to apply himself specially to the organic side of the science, may attend during his second and third years the Courses on Organic Chemistry, and courses on the Coal Tar Colours and on Dyeing and Printing.

Part of the Laboratory practice in the second and third years will consist in the examination and analysis of raw materials, products from chemical works, &c., in connection with the special courses of lectures on Applied Chemistry. In the Chemistry and Physical laboratories the practical work in the second year will be arranged in accordance with the branch of Chemistry selected by the candidate.

In the third year the student, if sufficiently advanced, will be set to work on some analytical process or problem in Applied Chemistry, under the direction of the teaching staff.

UNIVERSITY COLLEGE, NOTTINGHAM.

DEPARTMENTS OF CHEMISTRY AND METALLURGY.

Professor of Chemistry—F. Stanley Kipping, Ph.D., D.Sc., F.I.C., F.R.S.

Demonstrators of Chemistry—J. J. Sudborough, D.Sc., Ph.D., F.I.C., and R. M. Caven, B.Sc., F.I.C.

The Classes of the College are open to students of both sexes above sixteen years of age.

The Session commences on October 9th.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Elementary Inorganic Chemistry. In his second year he attends Lectures on both Inorganic and Organic Chemistry. In his third year he attends courses on Advanced Organic Chemistry, Physical Chemistry, and Advanced Inorganic Chemistry.

The fees for the Day Lectures and Classes are as follows: First year, two Lectures per week, 15s. per term. Second year, three Lectures per week, 22s. 6d. per term. Third year, four Lectures per week, 30s. per term.

Demonstrations and Lectures on Analytical Chemistry will be given in the day and evening, and should be attended by all students.

A Chemical Calculation Class is also held. Fee per Term, 5s.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry and Metallurgy.—The Chemical and Metallurgical laboratories are open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1; also on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Metallurgy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees for day students: For one term, £7; for the session, £18; for six hours weekly 40s., and 5s. extra for each additional hour per week. For evening students, 10s. for two hours per week, three hours 15s., four hours 20s., per term.

Research Work.—Students or others wishing to undertake research work in pure or Applied Chemistry will be afforded every facility for doing so and may be admitted at reduced fees. The Laboratories are fully equipped with apparatus and chemicals necessary for such work.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students can at all times work in the Chemical Laboratory, taking work suitable for the preparation for the Minor and Major Examinations. Special lectures will also be given in Chemistry and Materia Medica.

Government Lectures and Classes.—Evening Lectures and Laboratory instruction will be given by the Demonstrators of Chemistry to Students who intend to present themselves for Examination by the Government Science and Art Department in May next. Inorganic, organic, and practical chemistry, agricultural chemistry, and metallurgy will be taught in the elementary, advanced, and honours stages, each of which commences at the beginning of the College Session in September. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

An Agricultural Course of instruction, extending over two years, is now organised under the general direction of Mr. M. J. R. Dunstan, M.A., F.R.S.E. It includes instruction in chemistry, botany, agriculture, with practical work on experimental fields, dairy work, farriery, land surveying, &c. The instruction is designed for those who intend to become farmers, bailiffs, land agents, or colonists, and may be extended to a third year if desired,

Fee, £15 per annum for residents in Notts, £20 to residents in other counties.

Full information concerning all College Classes is given in the College Prospectus, price one penny.

UNIVERSITY COLLEGE, SHEFFIELD.

Professor of Chemistry—W. Carleton Williams, B.Sc., F.C.S.

Lecturer—G. Young, Ph.D., F.R.S.E.

The Session will commence on October 6th.

Beginners' Course.—Inorganic Chemistry: Tuesday from 10 to 11 a.m. Fee, £1 11s. 6d.

Matriculation Course.—Friday 10 to 11. Fee, £1 11s. 6d.

Intermediate Course.—Inorganic Chemistry. Monday and Thursday from 10 to 11 a.m. £2 12s. 6d.

Organic Chemistry.—Elementary: Saturdays, 10 to 11; fee, £1 11s. 6d. Honours: Tuesdays and Thursdays, 12 to 1; fee, £2 12s. 6d. Advanced: Thursdays, 4 to 5; fee, £1 11s. 6d. Special Course: Hours to be arranged; £1 1s. Chemistry of the Colouring Matters: Fridays, 12 to 1; fee, £1 11s. 6d.

Physical Chemistry.—Tuesday, 11 to 12. Fee, £1 11s. 6d.

Chemical Philosophy.—Thursday, 11 to 12. Fee, £1 11s. 6d.

Short Courses of Lectures are also given by L. T. O'Shea on the Chemistry of Coal Mining.

A Course of Lectures is arranged for Medical Students, with a special class in Qualitative Analysis.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Six hours per week, £5 5s.; Nine, £7; Twelve, £8 8s.; Eighteen, £11 5s.; Twenty-four, £14; Thirty-two, £17.

Day Students may not enter for less than six hours a week. Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

Fees for short periods (working thirty-two hours per week):—For one month, £3 3s.; two months, £5 5s.

An arrangement has been entered into with the Science and Art Department, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Department being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Evening Classes.—Lectures, Wednesday, 8 to 9. Laboratory instruction, Wednesday, 6 to 9, and another series to be arranged if desired. Sessional Fee, one evening per week, £1 10s.; two, 50s.; or Lecture Class and Laboratory, on Wednesday evening, £1 10s. Fee for one term, 17s. 6d.

UNIVERSITY COLLEGE, DUNDEE.

UNIVERSITY OF ST. ANDREWS.

Professor of Chemistry—James Walker, Ph.D., D.Sc.

Assistant Lecturers—J. S. Lumsden, Ph.D., B.Sc., and J. K. Wood, M.Sc.

Lecture Assistant and Laboratory Steward—J. Foggie, F.C.S.

The Winter Session begins on October 11th, and ends on March 21st. The Summer Session extends from the middle of April to the end of June.

The First Year's Lecture Course on Systematic Chemistry is given daily during the Winter Session, and embraces the Elements of Inorganic and of Organic Chemistry.

Advanced Courses, of about fifty lectures each, will be given during the year as follows:—

Organic Chemistry; Inorganic Chemistry, including the more important technological applications; Theoretical and Physical Chemistry; Bleaching and Dyeing, including the Chemistry of the Textile Fibres.

A special course of Physical Chemistry will be given during the Summer Session, 1900, including daily Lectures and Practical Laboratory Work.

Practical Instruction in all of the above branches will be given in the Laboratories and Dye-house. Special facilities are afforded to Research Students.

The Lectures and Laboratory Practice in Chemistry are recognised by the Medical Colleges of London and Edinburgh. The Courses are suitable for the degrees of the University of London and for the Civil Service appointments, and will also satisfy the requirements of Students in Pharmacy, and of Students who intend to become candidates for the Associateship of the Institute of Chemistry, as far as qualification in Chemistry is concerned.

UNIVERSITY OF EDINBURGH.

DEPARTMENT OF CHEMISTRY.

Professor—Alex. Crum Brown, M.D., D.Sc., F.R.S.

Lecturers—L. Dobbin, Ph.D., and H. Marshall, D.Sc.

Assistants—W. W. Taylor, M.A., B.Sc., J. P. Longstaff, and J. W. Eastham, B.Sc.

The working terms are—Winter Session, from middle of October to middle of March; Summer Session, from beginning of May to end of July.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical and science students is given by the Professor. The class meets daily; fee £4 4s. An Advanced Course of twenty-five lectures is also given in the Winter Session; fee, £2 2s. A class on Organic Chemistry is held in summer; fee, £2 2s. There is also a class on Chemical Theory, by Dr. Dobbin; fee £1 1s.; and a class on Mineralogy and Crystallography, by Dr. Marshall; fee, £2 2s. All these Lectures, except the General Course, are now open to women.

In addition to the above, Lecture Courses are given by the Assistants on some particular branch of Organic and Inorganic Chemistry. These Lectures are free to Laboratory Students.

Tutorial classes are held in connection with the General Course.

Laboratories.—Practical classes for Medical Students meet daily during the latter part of the Winter Session and in the Summer Session. (Fee, £3 3s.) The laboratories for analytical and advanced practical work are open daily from 9.30 till 4.30. (Fees: Whole Day—Winter Session, £10 10s., Oct.-Dec., Jan.-March; or Summer Session, £5 5s. Half Day—Winter Session, £6 6s., Oct.-Dec., Jan.-March; or Summer Session, £3 3s. Preference will be given to students in the above order. Students who are not Matriculated may attend the Chemical Laboratory on payment of the entrance fee of 5s. in addition to the Laboratory fees. Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry, including Gas Analysis, Metallurgy, and Assaying. Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical languages, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Final B.Sc. Examination includes

any three or more of the following subjects:—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy, including Anthropology, Physiology, Geology, including Mineralogy, Zoology, including Comparative Anatomy, and Botany, including Vegetable Physiology. In the Final Examination two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed; the same regulations apply also to the Practical and Oral Examinations. Chemistry in this examination embraces Inorganic, including Mineralogical, Chemistry; Organic Chemistry; Chemical Crystallography; History of Chemistry. Practical Examination:—Complex Qualitative Analysis; Inorganic and Organic Preparations; Gravimetric and Volumetric Analysis. Each candidate taking the higher standard will also be examined on any two of the following subjects, selected by himself:—Ultimate Organic Analysis; Gas Analysis; Assaying; Physico-chemical Measurements.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry may be required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—F. Grant Ogilvie, M.A., B.Sc., F.R.S.E.

Professor—John Gibson, Ph.D., F.R.S.E.

Assistant Professor—Allan W. C. Menzies, M.A., B.Sc.

Demonstrators—Andrew F. King and Ralph Marshall.

The Session begins October 3rd, 1899.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

Chemistry.—The first course for day students is a combination of Lectures with Laboratory instruction. In the Lectures some of the more important elements and their compounds are discussed in detail, so as to lead to a knowledge of the general laws of chemical action. Other important elements are treated in less detail, and the relations and classification of the elements generally are broadly indicated. In the Laboratory each student will receive instruction in general chemical manipulation, in accurate weighing, volumetric measurements, and in some of the simpler methods of quantitative analysis. After making a series of simple preparations, he works through a number of experimental exercises illustrating chemical combination, oxidation, reduction, and double decomposition. These exercises are followed by instruction in simple methods of qualitative analysis, especial attention being given to dry way testing and the use of the spectroscope. Students attending a further course may take up the study of systematic analysis, and extend the knowledge they have gained of quantitative analysis by exercises in gravimetric, volumetric, and electrolytic methods. Ultimately they may make a speciality of any branch of the subject which may be most necessary for their future work. Great attention has been paid to the thorough equipment of Advanced Laboratories, and special facilities are given to advanced students who may wish to engage in any class of Research (Inorganic or Organic) whether of a purely chemical or of a technical nature.

The teaching in the Evening Classes is based on the Syllabus of the Science and Art Department, and includes Elementary, Advanced, and Honours Courses in Theoretical and Practical Inorganic and Organic Chemistry.

GLASGOW AND WEST OF SCOTLAND
TECHNICAL COLLEGE.

Professor of Chemistry—G. G. Henderson, D.Sc., M.A.

Professor of Technical Chemistry—E. J. Mills, D.Sc., F.R.S.

Agricultural Chemistry Lecturer—John W. Paterson, B.Sc., Ph.D.

Professor of Metallurgy—A. Humboldt Sexton, F.C.S., F.R.S.E.

Also, Professors and Lecturers in the other leading branches of Pure and Applied Science and Technology.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan's Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments.

Complete courses of instruction are provided in both Day and Evening Classes.

Copies of the Calendar for 1899-1900 may be had from Mr. H. F. Stockdale, the Secretary, 38, Bath Street, Glasgow, price by post, 1s. 4d. Prospectuses will be sent free.

UNIVERSITY OF ST. ANDREWS.

UNITED COLLEGE OF ST. LEONARD AND ST. SALVATOR.

Professor of Chemistry—T. Purdie, B.Sc., Ph.D., LL.D., F.R.S.

The Session begins on October 11th. A Competitive Examination, open to intending Students of Arts, Science, and Medicine, for about sixty-four Entrance Bursaries, ranging in value from £40 to £2 15. each per annum, will be held on September 29th and following days. Forty-six of these Bursaries are restricted to Men and about fourteen to Women, the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine. Two of £40 each, and two of £30 each the first year of tenure and £40 the second year, are open to students of either sex. Two Scholarships of £100 each, tenable for one year, will be open for competition to Graduates of Science at the close of Session 1899-1900. A Hall of Residence is provided for Women Students. Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree; the regulations will be found in the "University Calendar."

Lecture Courses.

Two distinct Courses of Lectures are given, each comprising at least one hundred meetings of the class.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general

educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment. The Lectures are supplemented by a short Course of Laboratory Practice, intended to illustrate the principles of the science.

These courses of instruction are intended to meet the requirements of the Arts' Curriculum; also of candidates for the First B.Sc. Examination, and of students of medicine, so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part treats of the General Principles and Theory of Chemistry, and of more advanced Inorganic Chemistry, the instruction in general being such as is required for the Second B.Sc. Examination.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £3 3s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis; (3) Original Investigation. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the First and Second B.Sc. Examinations, and for Students of Medicine.

The fees for Practical Chemistry vary according to the number of hours taken weekly. A certain number of working places in the Laboratory will be available without fee for students who are capable of undertaking original investigation.

QUEEN'S COLLEGE, BELFAST.

Professor—E. A. Letts, Ph.D., D.Sc., F.R.S.E., &c.

I.—*Chemistry.*—The lectures are delivered at 3 p.m., on the first five days of each week, and terminate at the end of March. The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry. Fee, £2.

II.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of conducting Chemical Analyses. Fee, £3.

III.—*Laboratory Pupils.*—The Chemical Laboratory is open from November until the end of March, and from May 1st until the third week of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

Scholarships.—In addition to various Scholarships awarded in the Faculties of Arts and Medicine in which Chemistry forms a part of the examination, there are other valuable Scholarships awarded specially in connection with the schools of Chemistry and Physics.

QUEEN'S COLLEGE, CORK.

Professor—Augustus Edward Dixon, M.D.

Demonstrator—Robert Elliott Doran, F.C.S.

The College Session begins on October 17th, 1899, and ends on June 9th, 1900. The classes are open to male and female students.

Systematic Chemistry.—(1) General course of Inorganic Chemistry, Elementary Organic Chemistry, and Chemical Philosophy.—Fee for each Sessional Course, £2. Each subsequent Course, £1. (2) Advanced Organic Chemistry, and Chemical Philosophy.

Practical Chemistry.—(1) Two ordinary Courses of Practical Chemistry will be held, each of three months' duration; one commencing on January 5th, 1900, and adapted to the requirements of Students proceeding to the Examinations of the Royal University of Ireland; the other ending about the third week in June, and suitable for Medical Students intending to present themselves for the Examinations of other Licensing Bodies. Fee for each Sessional Course, £3. (2) A Course for Pharmaceutical Students will be held in the second and third terms; fee, £5. (3) Special Courses.

The Chemical Laboratory is open daily from 10 to 4 o'clock (except during class hours and on Saturdays) under the Superintendence of the Professor, to Students entering for special courses of qualitative and quantitative analysis; organic chemistry; or for the purpose of original investigation.

QUEEN'S COLLEGE, GALWAY.

Professor—Alfred Senior, Ph.D., M.D., F.I.C.

Demonstrator—W. S. Mills, B.A.

The College Session, 1899-1900, commences October 17 and ends June 9.

Chemistry is studied by attendance at Lectures, by work in the Laboratories, and by the use of the College Library. The Courses in the several faculties are arranged with a view to the requirements of the Royal University of Ireland, but are adapted also to those of other Universities and licensing bodies.

Lecture Courses. Faculty of Arts.—1. Second year's Course, Inorganic and the Elements of General Chemistry. 2. Third year's Course, Advanced Organic Chemistry. 3. Fourth year's Post-Graduate Course, Advanced General Inorganic and Organic Chemistry. *Faculty of Medicine.*—First year's Course, Inorganic and Elementary Organic Chemistry. *School of Engineering.*—First year's Course, Inorganic Chemistry.

Laboratory Courses. Faculty of Arts.—1. Second year's Course, Exercises in Inorganic Qualitative Analysis. 2. Third year's Course, Quantitative Analysis and other experiments to suit the requirements of individual Students. 3. Fourth year's Post-Graduate Course, Advanced Quantitative Analysis, Organic and Inorganic Preparations, and determination of their Physical and Chemical characters. 4. The Laboratories are also open to Students for work in other branches of Chemistry. *Faculty of Medicine.*—1. Second year's Course, Inorganic and Organic Elementary Qualitative Analysis, and the Chemical Examination of Urine. *School of Engineering.*—1. Second year's Course, Inorganic Qualitative Analysis.

A Scholarship in Chemistry is offered for competition each year of the value of £40, and Chemistry enters into the subjects required for numerous Scholarships in Arts, Medicine, and Engineering. The Royal Commission for the Exhibition of 1851 offer a Scholarship of £150 per annum. This Scholarship is at present held for a second year by a Chemistry Student of this College.

For Fees, Regulations as to Scholarships, and other particulars apply to the Registrar, from whom the Calendar, published in December, and the Extracts from Calendar, published in advance in July, may be obtained.

ROYAL COLLEGE OF SCIENCE FOR IRELAND, STEPHEN'S GREEN, DUBLIN. (SCIENCE AND ART DEPARTMENT).

Professor of Chemistry—W. N. Hartley, F.R.S.

Assistant Chemist—Hugh Ramage, F.I.C., Associate of the Royal College of Science, Dublin.

Demonstrator of Chemistry and Assaying—J. Holms Pollok, B.Sc.

The Session commences on Tuesday, October 6th, 1898.

The Royal College of Science for Ireland supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Mining, Engineering, and Manufactures, Physics, and Natural Science. If accompanied by a certificate from the Professor of Chemistry, the Diploma of Associate of the Royal College of Science in the Faculty of Manufactures is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry; (2) Advanced Chemistry, including Chemical Manufactures and Metallurgy; (3) Analytical and Experimental Chemistry; (4) Instruction in Chemical Research.

Fees payable by Non-Associate Students:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£2 for a special course of one month; £5 for three months; £9 for six months; £12 for the entire session. For Assaying—£5 for three months; £9 for six months; £12 for the entire session.

The following are supplementary courses of instruction:—

- (1) Laboratory Instruction in the Theory of Chemistry.
- (2) An Analytical Course for Students in Engineering.
- (3) A Course of Practical Chemistry for Medical Students.
- (4) The Analysis of Water, Air, Food, and Drugs, intended for the instruction of Public Analysts and Medical Officers of Health.
- (5) Assaying.
- (6) A Course of Chemistry for Pharmaceutical Students.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College. There are also nine Royal Exhibitions attached to the College, of the yearly value of £50 each, with Free Education, including Laboratory Instruction, tenable for three years; three become vacant each year, and are competed for at the May Examinations of the Department of Science and Art.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

CITY AND GUILDS OF LONDON INSTITUTE FOR THE ADVANCEMENT OF TECHNICAL EDUCATION.—The operations of the City and Guilds of London Institute are divided broadly into four branches: the educational work of three London Colleges, and of the Technological Examinations. Programmes of the London Colleges may be had on application to the Head Office of the Institute, Gresham College, Basinghall Street, London, E.C., or from the respective Colleges. The Technological Examinations (Examinations Department, Exhibition Road, S.W.), are conducted once every year at various centres throughout the kingdom. Programme, with Syllabus of Subjects, &c., may be obtained of Messrs. Whittaker and Co., Paternoster Square, London, or through any bookseller, price 10d., net.—*City and Guilds Technical College, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph.D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of productive industry, whether Manufactures or Arts. The main purpose of the instruction given is to practically demonstrate the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The

courses of instruction are arranged to suit the requirements of—1. Persons who are training to become Technical Teachers; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. The Matriculation Examinations will begin on Tuesday, Sept. 19th, and the Winter Session opens on Tuesday, October 3rd. *City and Guilds Technical College, Finsbury*.—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in special subjects. An examination for the admission of Students will be held at the College at 10 o'clock on Tuesday, September 19th, 1899. *South London Technical Art School*.—Classes in Modelling, Design, Drawing and Painting from the Life, and House Decoration.

CITY OF LONDON COLLEGE, White Street, Moorfields.—Courses of Evening Lectures and Laboratory Practice in Chemistry and Physics, conducted by Mr. I. S. Scarf, F.I.C., F.C.S., assisted by Messrs. H. W. Harrie, F.C.S., and C. A. West, A.R.C.S., F.C.S. Session commences September 25.

BATTERSEA POLYTECHNIC.—Principal, Mr. Sidney H. Wells, Wh. Sc. Inorganic, Organic, and Technological Chemistry, Mr. John Wilson, M.Sc. (Vict.), assisted by Mr. John L. White, M.Sc., and Mr. B. C. Polkinghorne, B.Sc. Day and Evening Classes in Science and Art subjects.

BIRKBECK LITERARY AND SCIENTIFIC INSTITUTION, BREM'S BUILDINGS, CHANCERY LANE.—Chemistry Courses will be conducted, commencing September 26, adapted for the Elementary, Advanced, and Honours Examinations of the Science and Art Department, and for the Matriculation, B.Sc., and M.B. Degrees of the London University, by Mr. J. E. Mackenzie, Ph.D., B.Sc.

BOROUGH POLYTECHNIC INSTITUTE, 103, Borough Road (near the Obelisk).—Chemistry: Evening Lectures and Laboratory Work (Session fees, per course, 3s. to 15s.), Dr. F. Mollwo Perkin, assisted by Dr. A. J. Walker. Physics: Evening Lectures and Laboratory Work (Session fees, per course, 6s. to 10s.), Dr. J. Henderson. Session opens Monday, September 25, 1899.

BRIXTON SCHOOL OF CHEMISTRY AND PHARMACY, 12, Knowle Road, Brixton.—Dr. A. B. Griffiths, F.R.S.E., F.C.S., &c. The Lectures and Classes are adapted to the requirements of Pharmaceutical and Medical Students, and also those who are proceeding to Degrees at the University of London. Medals and certificates are awarded to successful students. The Laboratory is fitted with every convenience for the prosecution of chemical studies and research. Prospectuses and further information may be obtained from the Principal.

SOUTH - WESTERN POLYTECHNIC, Manresa Road, Chelsea.—Principal, Herbert Tomlinson, B.A., F.R.S. Technical Day Classes in Chemical Industries, commencing September 25th.

THE GOLDSMITHS' INSTITUTE, New Cross, S.E.—Head of the Chemistry Department, Mr. W. J. Pope; Assistants, Mr. S. J. Peachey and others. Lectures and Practical Classes in General Chemistry, also in Chemistry applied to other industries, are held in the evenings from 7.30 to 10.0, and are open to both sexes. Special attention is paid to Technical Laboratory work and the investigation of manufacturing difficulties.

POLYTECHNIC INSTITUTE, 309, Regent Street, London, W.—Mr. R. A. Ward and Assistants.—Evening Classes in Theoretical and Practical Chemistry, &c.. The Classes are open to both sexes.

NORTHERN POLYTECHNIC INSTITUTE, Holloway, N.—Principal, J. T. Dunn, D.Sc. Evening Classes in Theoretical and Practical Chemistry. Assistants, Mr. H. Charles L. Bloxam and Mr. W. H. Watson, A.R.C.S.

CARPENTERS' COMPANY TECHNICAL INSTITUTE, Jupp Road, Stratford, E.—Principal, William Ping, F.C.S. Session begins—Day Classes, September 11th; Evening Classes, September 25th. Evening Classes in Theoretical and Practical Chemistry, and in many other Departments of Science and Art. Day Technical School.

EAST LONDON TECHNICAL COLLEGE, People's Palace, E.—Chemistry: Professor, J. T. Hewitt, M.A., D.Sc., Ph.D.; Demonstrator, F. G. Pope; Assistants, H. A. Phillips and A. J. Turner. Lectures and Practical Classes are held in the daytime in connection with the three years' course of the Day Technical College. Evening Classes are also held, offering instruction in the courses of the Science and Art Department and for the examinations of the University of London.

UNIVERSITY TUTORIAL COLLEGE, 32, Red Lion Square, Holborn, W.C. (Science Department of the Univ. Corr. Coll.).—The next Session commences on Monday, October 2nd. Work may be taken up in the Laboratories for short periods, or in systematic classes extending for one or more terms. Special facilities are offered to country students for work during the ordinary vacations. During last year, students of University Tutorial College carried off over £1000 in Hospital and Entrance Scholarships, and at the recent Science Examinations (July, 1899) of London University, no less than 155 students were successful.

SOUTH LONDON SCHOOL OF PHARMACY, Lim., 325 and 409, Kennington Road, S.E.—Lectures on Chemistry and Physics, by Dr. John Muter, F.R.S.E., F.I.C., and Mr. J. Thomas, B.Sc. (Lond.), Daily, at 12 noon. Lectures on Botany daily at 11 a.m. by Dr. Muter, and at 2.30 p.m. on Materia Medica and Pharmacy, by Dr. Kingan, M.P.S. The Students' Laboratory of this Institution is specially designed to accommodate 40 Students. The Technical Laboratory is open daily from 9 till 5, and is fully fitted with all apparatus for teaching the manufacture of drugs and chemicals. Periodical Examinations of the Students are held by Visiting Examiners appointed by the Council of Education, and Medals and Certificates are awarded on the results thereof. Fees: for the first term, 12 guineas; for the second term, 8 guineas; and for the third 7 guineas; afterwards 2 guineas per month, inclusive of all departments. A special laboratory for training Advanced Students in Analytical Chemistry under the care of Mr. A. H. Mitchell Muter, A.I.C., F.C.S.

IMPERIAL COLLEGE OF CHEMISTRY AND PHARMACY, 51, Imperial Buildings, Ludgate Circus.—Mr. F. Davis, B.Sc. An especial course of instruction has been organised for Fellows and Associates of the Institute of Chemistry to meet the requirements of the Local Government Board in Therapeutics, Pharmacology, and Microscopy, as recommended by the Council of the Institute.

METROPOLITAN COLLEGE OF PHARMACY, 100 and 162, Kennington Park Road, S.E.—Principal, W. Watson Will, F.C.S.

WESTMINSTER COLLEGE OF CHEMISTRY AND PHARMACY, Trinity Square, Borough, S.E.—G. S. V. Wills, Principal; E. Walden, Secretary.

COUNTY BOROUGH OF BOLTON PUBLIC LABORATORY, Albany Chambers, 21, Mawdsley Street, Bolton.—Special instruction in the Analysis of Foods and Drugs, and in Commercial and Applied Chemistry, Assaying, &c. Apply, Walter Ratcliffe, F.C.S., Principal.

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NOTE ON BUTTER ANALYSIS.

By W. LAWRENCE GADD, F.I.C.

ONE of the most valuable and widely used methods of examining butter is the determination of the amount of alkali required to neutralise the volatile fatty acids, originally due to Reichert. As the figures afforded by this method of analysis commonly determine, to a large extent, whether adulteration is indicated or not, it is of the first importance that the process should be as free as possible from any source of error; and, furthermore, should, under similar conditions, give the same results in the hands of different analysts.

A recent experience in connection with a sample of butter suspected of adulteration, showed that exactly concordant results are not always obtained by two or more chemists working on the same sample when the estimations are carried out in the usual manner. This led me to undertake some experiments, which are not yet complete, but the first results of which justify the publication of this note.

In Reichert's test, as ordinarily carried out, the saponification of the butter fat is effected by heating with approximately semi-normal alcoholic potash, prepared from methylated spirit which has been re-distilled with caustic potash. This solution, as is well known, is liable to change with age, even when kept in closely stoppered bottles, and it occurred to me that this might be a source of error in making the Reichert test.

To ascertain this, a solution of caustic potash in alcohol (A) was carefully prepared in the usual way, and stored in a well-stoppered bottle. Another similar solution (B) was also prepared and kept in a flask, which was loosely closed by an ordinary cork, for three weeks before using. This solution rapidly darkened in colour (by oxidation) and became much the darker of the two solutions. The Solution A was employed at intervals of a few days to estimate the volatile fatty acids in a sample of butter fat carefully prepared from genuine butter, and gave numbers ranging from 14 c.c. to 12.2 c.c. Solution B, after keeping for three weeks, gave, with the same sample of butter fat, 19.3 c.c. to 20.6 c.c. for 2.5 grms. of fat.

Side by side with each of these determinations, an estimation was made on the same butter fat in the following manner:—

About 2.5 grms. of the butter fat (which should be only just melted, and on the point of solidification) is accurately weighed in an 8-oz. flask; 20 c.c. of methylated spirit, freshly distilled with caustic potash, and about 1 gm. of solid potassium hydrate, are added, and the flask plunged into hot water. The potash rapidly dissolves in the alcohol, and the butter fat is saponified in a very short time. The flask is heated in the water-bath until all trace of alcohol is evaporated off, filtered air being blown in from time to time, and the soap spread evenly over the inner surface by turning the flask round and round to facilitate the evaporation.

When all smell of alcohol is gone, 50 c.c. of distilled water are added, and the soap dissolved by gently heating the flask on the water-bath. After cooling the solution, 20 c.c. of a 10 per cent solution of pure sulphuric acid are then added, together with a few pieces of broken porcelain, the flask attached to a condenser, and exactly 50 c.c. distilled off. The distillate is filtered, the receiver and filter washed two or three times with warm water, and the

filtrate titrated with N/10 sodium hydrate, using a single drop of phenolphthalein as indicator.

By this method it was found that practically the same results were given by a sample of butter fat after forty days' keeping as when freshly prepared, although in the interval the fat had changed slightly and had become bleached perfectly white. The following are the actual results obtained:—

Age.	Alcoholic potash.			Solid caustic.		
	Fat taken.	N/10 NaOH required.	N/10 NaOH for 2.5 grms. fat.	Fat taken.	N/10 NaOH required.	N/10 NaOH for 2.5 grms. fat.
Days.		C.c.	C.c.		C.c.	C.c.
Solution A.						
1	2.564	13.0	12.6	2.560	16.0	15.6
7	2.517	14.1	14.0	2.516	16.4	16.2
11	2.551	13.8	13.5	2.559	16.5	16.1
13	2.552	12.8	12.5	2.529	16.3	16.1
16	2.527	12.4	12.2	2.527	16.5	16.3
Solution B.						
23	2.515	19.3	19.1	2.577	16.3	15.8
39	2.552	21.1	20.6	2.501	16.0	15.9
45	2.533	21.0	20.7	2.555	16.4	16.0

From these figures, it will be seen that the change undergone by alcoholic potash on keeping has a serious effect upon the accuracy of Reichert's test, and, in extreme cases, probably renders the estimation valueless. On the other hand, by using fresh alcohol and solid potash in the manner described, concordant results are obtained even with fat several weeks' old.

THE ANALYSIS OF BINARY ALLOYS.

ABOUT two years ago an attempt was made to analyse some brasses, without separating the copper and zinc, by taking advantage of the respective behaviour of the two metals with standard potassium cyanide in an alkaline solution. By completely discharging the blue colour of the ammoniacal copper solution, and then adding potassium iodide, and going back with silver nitrate to a faint silver iodide turbidity (CHEMICAL NEWS, lxxvi., p. 189), the copper, when alone, was accurately estimated, but the zinc, unfortunately, under the above conditions, was so very irregular in its indications that the alloys in question had to be analysed by other means.

The principle of the process seems to have some merit, and as I am unaware of its having been previously suggested I venture to give it here, in the hope that some one may have an occasion to make use of it, my own opportunities of doing so, at present, not being apparent.

Let A and B be the two constituents of the alloy, and X and Y the amount of standard solution they respectively utilise. Let M c.c. be the amount of solution the weighed amount of alloy actually needed, and M' the calculated amount it would need if it all happened to be A; also let the ratio—determined, if necessary, by experiment—between equal weights of A and B be R. Then,—

$$X + Y = M \text{ and } X = M - Y,$$

but—

$$Y = \frac{M' - X}{R};$$

so—

$$X = M - \frac{M' - X}{R} = \frac{MR - M'}{R - 1}$$

The same conclusion is reached by regarding—

$$X = M - \frac{M' - M}{R}$$

as an approximate expression, and then continually substituting for the asterisked M the value—

$$M = \frac{M' - M^*}{R},$$

and summing the series.

This very clumsy way is the one in which I first worked out the expression—

$$X = M - \frac{M' - M}{R - 1},$$

which is identical with—

$$\frac{MR - M'}{R - 1}.$$

If $R = 1$ the process is valueless. It becomes increasingly accurate as R differs from 1; supposing, of course, the titrations remain equally reliable.

J. T.

ON THE PURIFICATION OF ACETYLENE BY MEANS OF ACID SALINE SOLUTIONS.

By ALBERT R. FRANK.

IN a recently published paper (*Zeit. f. Angew. Chem.*, Nos. 40-41, 1898), Dr. Wolff passes in review the methods of purifying acetylene which give the best results. In the first place we find that of Lunge and Cederkreutz, improved by this author (Dr. Wolff), a process which depends essentially on the oxidation by chloride of lime of the impurities which accompany acetylene. He also describes the process I proposed, which consists of using acid saline solutions to absorb the impurities; then the ammonia is neutralised by the acid, while the sulphuretted hydrogen is precipitated in the state of metallic sulphide, and the phosphoretted hydrogen is absorbed.

Wolff gives the preference to his process, since, according to him, the use of acid saline solutions has great drawbacks, but it is not at all necessary to use saline solutions in the liquid state; it is, on the contrary, preferable to impregnate porous bodies, especially kieselguhr, with these solutions; in this manner the volume occupied by the purifying material is very much diminished, and the method is particularly adapted to small plants. The above-mentioned author seems to think that by using my method the choice of apparatus would present certain difficulties, and he is of opinion that the use of metallic vessels should *a priori* be condemned. He is, however, in error; in most branches of chemical industry apparatus of enamelled iron has for a long time been used, and has given every satisfaction; they resist the action of the most concentrated acids, even when warm. It is also incorrect to imagine that acid saline solutions can cause explosions; this might apply to solutions of copper, on account of the formation of acetylide of copper, but my solutions are prepared in such a manner that the copper is precipitated in the state of sulphide long before the whole of the acid becomes neutralised by the ammonia, even if the latter be present in the gas in very large proportions.

The purifying material consists of a very acid solution of cuprous chloride, or of an acid solution of ferric chloride of known strength; and these solutions do not attack, neither do they decompose, the acetylene gas in any way. One kilogram. of ferric solution is enough to purify 7 to 10 cubic metres of acetylene, and the same quantity of the cuprous solution is enough to purify 18 to 25 cubic metres of this gas without being exhausted. Further, in the case of cuprous solutions, the exhausted purifying material can be easily regenerated.

It suffices to boil the cuprous solution after having freed it from the precipitate of cuprous sulphide; in this manner we can eliminate the phosphoretted hydrogen, which is never found in the state of phosphide, but simply

in a state of rather unstable combination, easily decomposable by heat. The solution is now ready to use again after a certain amount of copper has been added, and it has been brought up to its original volume by means of hydrochloric acid.

When we have to deal with, as has generally been the case up till now, an acetylene apparatus supplying 20 or 30 lamps, each burning five or six hours a day, and each consuming 20 litres of gas an hour, it suffices to have a purifying apparatus capable of holding 12 to 15 kilograms. of purifying material. This quantity is enough to last three or four months, and when it commences to become exhausted we notice a diminution of the lighting power, and the formation of phosphoric acid, and sulphuric and anhydride fumes. Even when the material no longer absorbs phosphoretted hydrogen and sulphuretted hydrogen, there still remains a quantity of acid more than sufficient to absorb the whole of the ammonia, and the formation of easily decomposable metallic acetylides is impossible.—*Zeitschrift für Angewandte Chemie*, 1898, p. 1050.

ON THE COMPOSITION OF THE FATTY OIL EXTRACT OF CEDAR NUTS.

By M. D. KRYLOFF.

CEDAR-NUT oil may become an important article of commerce in view of the abundance of the cedar forests in the northern districts of Russia in Europe, and Siberia. Unfortunately the exploitation of these forests is still in a very primitive state. At the exhibition at Nijni-Novgorod in 1896, the firm of Fedtcherxo and Gridassof exhibited some cedar oil, a sample of which has been used by the author for his experiments.

The sample examined was a thick transparent liquid, with a golden straw-yellow colour. Its density at 0° was 0.9326. At -20° the oil did not solidify, but simply became thicker.

The following table gives the constants of cedar oil compared with those of some other oils:—

	Index of iodine.	Reichert-Meissl index.	Saponification index.	Acid index.
Linseed oil ..	158—178	0.95	190—192	0.4—1.1
Cedar oil ..	149.5—150.5	2.0	191.8	1.09
Hemp-seed oil	143—144	—	192—194	0.64—4.82
Sunflower oil	19.9	0.5	193—194	—
Olive oil ..	81.6—84.5	1.5	191—193	1.66

We see that cedar oil does not differ much from other oils as regards its composition.

The fatty acids extracted from the oil gave a crystalline deposit which has been separated. The semi-solid mass was spread out on porous plates, and then re-crystallised several times in alcohol. This substance melts at 63°, and on analysis gives figures corresponding to the formula $C_{16}H_{32}O$. It was thus shown to be palmitic acid.

The liquid fatty acids which are found in the filtrate were oxidised with permanganate of potash, and the separated oxy-acids were purified by boiling in alcoholic solution with animal charcoal, and then fractionally crystallised; three fractions were thus obtained. Fraction I., the most considerable, melting at 165°; fraction II., melting at 159°—161°; and fraction III., the smallest, melting at 140°.

The first fraction consisted of tetroxy-stearic acid, and the last fraction of dioxy-stearic acid containing a small quantity of tetroxy-stearic acid.

The conclusion to be drawn from these experiments is that cedar oil resembles linseed oil with regard to its composition, and may be looked upon as belonging to the class of siccative oils.—*Journal Rouss Physico-Chim. Obchestechna*, 1898, p. 9248.

THE AFTER-FORMATION OF GAS IN ACETYLENE GENERATORS.

By P. WOLFF.

AN inherent fault in all acetylene generators is the after-formation of gas, which takes place after the direct contact between the carbide and the water has ceased. This generation is due to the action of the residual water contained in the pores of the carbide, to the condensation of water on the surface of this carbide, and also to the absorption of aqueous vapour.

The author has measured the quantity of gas thus liberated by 1 kilogram of carbide by passing it through a meter. In one series of experiments the carbide reservoir was over water; in other experiments it was over petroleum. The results showed that in the latter case the quantity of gas formed amounted to 0.25 litre at the end of the first half hour, to 6 litres after twenty-four hours, and then remained constant at 16 litres at the end of three days. In the first case, on the other hand, 7.5 litres were collected in half an hour, 25 litres in twenty-four hours, and 30 litres at the end of three days; after that, the liberation of gas continued at the rate of from 5 to 6 litres per day, until the integral decomposition of the carbide was complete.

These figures show in a very plain manner the considerable risks of explosion which are incurred by the use of small generators, and table lamps in particular. This danger can be avoided in large apparatus by using a reservoir of sufficient capacity to hold the excess of gas without undue compression.

Different means have been proposed for obviating this inconvenience, especially the use of a layer of petroleum to separate the carbide from the water; but this method is not practicable—for, on the one hand, a very thin layer of petroleum does not prevent the evaporation of the water; and, on the other hand, with a thick layer there would be a risk of close contact with the carbide, which would be then rendered impervious to water.

The most efficacious method appears to be that of Münsterberg. A valve closes all communication between the carbide reservoir and the water as soon as the former has been raised; the after-formation of gas is therefore no longer produced, except by the water contained in the pores of the carbide. Further, in Münsterberg's apparatus the gas reservoir is of large size, so that the proportion of air introduced at the same time as a fresh charge of carbide is no more than 20 per cent; that is to say, below the limit of explosive mixtures.—*Metallarbeiter*, xxiv. (16), p. 122.

ON THE PRESENCE OF AMMONIA IN RAW ACETYLENE.

By Dr. HEINRICH BAMBERGER.

FROM the point of view of their origin, the deleterious foreign bodies which accompany acetylene may be divided into two classes; the bodies which are derived from the raw materials used in the preparation of the carbide (phosphoretted hydrogen, sulphuretted hydrogen), and secondly, the bodies formed during the operation of electric fusion (ammonia and compounds of cyanogen). The presence of those first mentioned may be avoided, to a certain extent, by the use of raw materials of as great purity as possible, but as far as concerns ammonia it is necessary to take the very greatest precautions in the operation of fusion itself.

The injurious action of the ammonia contained in the acetylene is much greater than that exercised by phosphoretted hydrogen and sulphuretted hydrogen, for these two bodies are transformed during the combustion of the acetylene into nitro-oxygenated compounds. What we

therefore have to do is to eliminate this body, which is fortunately not at all a difficult operation.

During the decomposition of the carbide of calcium by water, the ammonia is formed at the expense of two different compounds, the nitrides and the cyanogenated compounds. The formation of nitrides is due to the presence of either aluminium or of magnesium in the lime.

Nitride of magnesium, Mg_3N_2 , is formed simultaneously with the oxide during the combustion of the magnesium; water decomposes it, even in the cold, into oxide and ammonia. It is true that up to the present we have not succeeded in finding magnesium in the carbide, but the magnesia contained in the lime is reduced by the electric current to the metallic state, and thus gives rise to the nitride.

It must be remembered that a certain quantity of air is always circulating through the electric furnace, and that the carbons, the crucibles, and the braizes always contain a certain quantity of nitrogen; this explains the formation of the nitride.

On the other hand, aluminium is found in greater or less quantities in almost every variety of lime, as well as in carbon, under the form of more or less impure alumina. In the presence of carbon, alumina is reduced to the metallic state, and the metal combines by combustion in air with the nitrogen. Like the corresponding compound of magnesium, nitride of aluminium also causes, under the same conditions, the formation of ammonia. The second source of this body is furnished by the compounds of cyanogen.

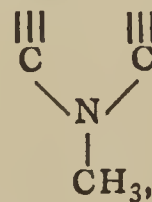
The carbides have the property of absorbing nitrogen at a high temperature, and of forming cyanogenated compounds. The formation of ammonia at the expense of these compounds is due to a saponification which takes place under the influence of superheated steam.

A large number of analyses have shown that acetylene contains from 0.05 to 0.15 per cent (by volume) of ammonia.—*Zeitschrift für Angewandte Chemie*, 1898, p. 720.

ON THE ACTION OF FUMING NITRIC ACID ON SOME CYCLIC COMPOUNDS OBTAINED BY SYNTHESIS.

By Dr. H. KUNZ-KRAUSE.

It has recently been shown that Vitali's reaction may serve to show the presence of the methylimide group,—



in the heterocyclic annular compounds, and also to what point it will serve for this purpose, and consequently for the recognition of the constitution of natural alkaloids.

Starting from this point, the author thought it would be of interest to extend his research to the so-called aromatic compounds, in which the atom of nitrogen does not form part of the ring, but serves as a lateral link of an isocyclic annular system. The anilines and anilides are compounds of this nature. The anilides, and first among them acetanilide, and the analogous compounds occupy, thanks to their recent employment in medicine, a place of great interest in pharmacy. It seemed advisable to apply the research to this group of bodies first of all.

The carrying out of the experiments referred to later on was effected in the manner described in the previous research on the subject of the reaction of carbylamine. As with these former, the following reactions have been obtained in every case, with 0.2 gram of material, and 3 c.c. of fuming nitric acid at 1.5 density, and by repeating

the experiment at least three times. In certain cases, and, above all, when the results were negative, these were checked by control experiments repeated several times. For performing these experiments, the same porcelain crucibles as used in the previous experiments were found to give the best results. The mixture was evaporated down on a boiling water-bath, and the residue was left until the reaction described further on took place. The observations made on each compound are taken into consideration in the following résumé.

When I commenced the series of experiments with acetanilide, I made the surprising observation that the product of the action of the acid, which existed in the form of a reddish-brown residue, was distinguished by a property which could hardly have been predicted by theory; this was its spontaneous inflammability. On this account it seemed advisable to first examine the anilides in this connection, and to endeavour to answer the following questions:—

1st. Should we find in this behaviour of acetanilide a characteristic reaction of value for its identification? or, 2nd, is it common to the other derivatives of acetanilide and to other anilides? Can we, in this case, find any relationship between the reaction and the constitution of the bodies in question?

Experiment has decided in the latter sense, as will be shown by a study of the results.

I would strongly advise that the experiments be carried out in a closed space, and that, as a precaution against violent inflammability, not more than 0.2 gm. of products liable to form spontaneously inflammable compounds should ever be used.

I. *Acetanilide*.—This body dissolves easily without any violent action, taking a greenish-brown colour. The reaction does not become stronger, except after the addition of relatively large quantities of fuming nitric acid. The latter part of the experiment is of greater interest. The original greenish-brown solution becomes a reddish-yellow, then a deep red, then brown, and, finally, when it is almost completely evaporated down, a very deep blackish brown. At this moment the residue suddenly takes fire, and a tall column of brilliant flame, charged with soot, shoots up from the crucible. The residue, after the extinction of the flame, has an odour of nitrophenol, which changes to that of aniline on the addition of an aqueous solution of soda-lye.

As this reaction is certain, even when we only use 0.14 gm. of acetanilide, and as, on the other hand, it does not take place with the analogous compounds recently used in medicine, with the exception of *p*-bromide of acetanilide, or *o*-tolylacetamide, it merits a certain amount of attention, from the practical point of view, as a sure and simple method of detecting this substance. Repeated trials with different quantities have proved that the reaction reaches its lower limit with 0.14 gm. of material, while with 0.15 gm. we always obtain a large flame; ignition no longer takes place with 0.13 gm. By using 0.14 gm. we always obtain a spontaneously inflammable residue, if the evaporation has been carried out in a porcelain crucible as has already been recommended.

II. *Acet-o-toluide (o-Methylacetanilide)*.—After a lively reaction, we immediately obtain an orange-yellow solution. The residue from the evaporation, which is spongy and of an orange-red colour, ignites spontaneously and burns, leaving a light spongy mass of carbon.

III. *p-Chloride of Acetanilide*.—Vapours of hyponitric acid are given off in large quantities from the orange-yellow solution, and suddenly a brilliant flame, charged with soot, shoots up from the crucible; the residue, unlike that from acetanilide, does not appear to be carbonised, but remains orange-yellow in colour, and continues to give off luminous vapours at short intervals, giving rise to fresh explosions, a characteristic test for the *p*-halogen-acetanilides (see the following compound).

The residue is a dry yellowish-brown mass. By using 0.14 gm. of the material and 3 c.c. of fuming nitric acid

I was enabled to observe nearly twenty spontaneous ignitions, the last one being particularly bright.

IV. *p-Bromide of Acetanilide*.—This body behaves in the same manner as *p*-chloride of acetanilide. With 0.20 gm. of material, three consecutive spontaneous ignitions were obtained. I would here mention a method, elaborated on the occasion of the present research, for the better preparation of this compound. It is certainly preferable to the ordinary method, which consists of introducing the calculated quantity of bromine into the acetic solution of acetanilide: we dissolve in a porcelain dish 12 grms. of acetanilide in 2 litres of water, heating gently. After cooling, an equally cold solution of 14 grms. of bromine in distilled water is added to the filtered solution until it becomes yellow. The precipitate of *p*-bromide of acetanilide is washed with cold water, and dissolved in boiling water to obtain pure crystals. The normal fusing point of the product thus obtained is 166°.

V. *p-Nitroacetanilide*.—This behaves in an analogous manner to that of the two *p*-halogen-acetanilides. By using 0.20 gm. of material, I noted an ignition of the brown residue from the evaporation, which was repeated three times.

VI. *Benzoanilide*.—The residue from the evaporation of the greenish-brown, and afterwards brownish-yellow solution, is of a soft consistency, and of an orange-red colour. It does not ignite spontaneously.

VII. *Acetylacetanilide*.—In spite of the great speed of the reaction, the yellowish-brown residue does not ignite spontaneously; this distinguishes it from the acetanilide. The introduction of a second acetyl group, in the arrangement of the atoms of the first, annihilates the inflammability of the nitrogen compounds of acetanilide.

VIII. *Methylacetanilide (Exalgine)*.—The solution, which is bright yellow, is easily obtained. After heating, there results, after a lively reaction, an olive-green solution. The syrupy brownish-yellow residue is not spontaneously inflammable.

IX. *Acet-p-toluide (p-Methylacetanilide)*.—The reaction is very violent, and is accompanied by a large disengagement of nitrous vapours. We immediately obtain an orange-red solution. The residue from the evaporation does not ignite spontaneously, but burns very fiercely on the approach of a flame.

X. *Acetyl-o-amidophenol*.—The reaction is impetuous, and produces a greenish-brown solution, which keeps on disengaging large quantities of vapour. The final residue does not ignite either spontaneously or on the approach of a flame.

XI. *Acetyl-p-amidophenol*.—This reaction, which is also very brisk, furnishes an orange-red solution, giving off large quantities of nitrous vapours, and the residue of which, after evaporation, is a greyish-yellow. It will not ignite either on the approach of a flame or spontaneously.

XII. *p-Methoxyacetanilide (Methacetine)*.—The residue from the evaporation of the solution does not ignite spontaneously, in spite of the violence of the reaction, accompanied by a considerable disengagement of nitrous fumes. It will only ignite, but then easily, on actual contact with a flame. Its colour is brownish-yellow.

XIII. *p-Ethoxyacetanilide (Phenacetine)*.—The action is extraordinarily violent. The product of the reaction, which is first a yellowish-red, then brownish-red, does not ignite spontaneously, and does not give off carbilamine either with an aqueous or alcoholic solution of potash. Treatment with an aqueous solution of potash lye produces an odour of fresh pears.

XIV. *Aceto-p-sulphanilate of Sodium (Casaprine)*.—The reddish-brown residue does not ignite spontaneously, but contact with a flame causes it to burn brilliantly, accompanied by a deposit of soot.

XV. *Acet-p-amidosatol (Salophene)*.—The brownish-black residue does not ignite spontaneously, but burns quietly, without forming soot, on contact with a flame.

XVI. *Oxalanilide*.—In spite of the violent reaction

which takes place on the addition of acid, it was not possible to obtain a spontaneous ignition of the pulverulent, white residue, even when using 0.5 gm. of material.

XVII. *α-Acetonaphthylamide*.—The solution obtained, after a very vigorous reaction, is of an orange-red colour; the residue from its evaporation does not ignite spontaneously, but only on contact with a flame, when it detonates and produces a large quantity of carbon and soot.

XVIII. *β-Acetonaphthylamide*.—This reaction, which is still more violent than the preceding one, produces a greenish-black solution, which gives off continuously hypnitric fumes. The residue only ignites on contact with a flame, and its combustion proceeds very quietly.

XIX. *Ethoxy-ana-benzoylamidochinolene (Analgene)*.—The reddish-yellow solution gives, on evaporation, an orange-red residue, with a very strong odour of benzoin. It does not ignite either spontaneously or on contact with a flame.

From the above it appears that of all the bodies examined up to the present there are, besides acetanilide itself, only the parachloride and parabromide of acetanilide, nitroacetanilide, and orthomethylacetanilide, which produce, by evaporation with fuming nitric acid, residues which ignite spontaneously.

We are able to deduce the following conclusions which are of great interest from the theoretical point of view:—

1st. Spontaneous ignition, which characterises the product of the reaction of fuming nitric acid on acetanilide under the conditions described above, takes place when strongly electronegative elements or molecules—Cl, Br, NO₂—are found in the para-position of the acetamide group. The same holds good for the group CH₃ in the ortho-position.

2nd. Spontaneous ignition does not take place—

- When the electro-positive groups—CH₃, OCH₃, OC₂H₅, or OH—or the molecules of SO₂ONa, or of the more complicated acids, C₆H₄ $\begin{smallmatrix} \text{OH} \\ \text{CO} \end{smallmatrix}$, are found in the para-position to the acetamide group.
- When the group OH takes the ortho-position to the acetamide group. This cannot, consequently, replace the CH₃ group.
- When the atom H, still unplaced in the acetamide group, is replaced by CH₃.
- When the acetyl molecule is replaced by another acid one; or, finally,
- When the benzoic nucleus is replaced by the naphthalene or chinolene nucleus—*Pharm. Zeit.*, Berlin, 1898, No. 94.

ANALYTICAL METHODS FOR DISTINGUISHING BETWEEN NITROGEN OF PROTEIDS AND NITROGEN OF SIMPLER AMIDES OR AMIDO-ACIDS.

By J. W. MALLET,
Professor of Chemistry, University of Virginia.

DISCUSSION OF MATERIALS AND CONDITIONS.

It is admitted by all who have had experience in the chemical analysis of materials used as food that the common practice of determining the total nitrogen in such materials, by multiplying the result by 6.25 and calling the product so obtained "protein," is but a crude and clumsy way of approximately representing the value of the material under examination as respects its nitrogenous constituents. Besides the substances which are properly designated as proteids, there are other nitrogenous constituents of food materials which differ widely from these in nutritive value, and some of which also differ greatly from these and from each other in the proportion of nitrogen which they contain.

Classes of Nitrogenous Constituents in Foods.

The following classes of the nitrogenous constituents of food are commonly recognised as requiring separate consideration:—

1. Proteids proper (by some called albumenoids), and their closely related derivatives, the proteoses and peptones.
2. Gelatinoids or collagens, and allied substances immediately derived from them, such as gelatin, chondrin, &c.
3. Simpler amides, amido-acids, and allied substances, such as the asparagin, glutamin, &c., of vegetable materials, and the "flesh bases" (creatin, creatinin, &c.), of animal origin.
4. Alkaloids, or amine-like compounds of well-determined basic character.
5. Ammonia and its salts.
6. Nitrates.

To these, no doubt, should be added lecithin and analogous substances containing nitrogen, but closely allied to the fats.

The known and commonly used methods for determining nitrogen in the forms of ammonia and nitrates, which occur but sparingly in food materials, may be considered fairly satisfactory. Alkaloids in the commonly accepted sense of the term demand attention only in connection with such special accessories of food as tea, coffee, and similar nervous stimulants, and the chief substances of alkaloidal character admit of being separately dealt with in these special cases without serious trouble and with a fair degree of accuracy.

It is with the first three of the above-named classes of food constituents that difficulty is encountered, and for which further study of methods is desirable. The object of the work which the writer has undertaken, and to which he has devoted a good deal of time for several months past, has been to study the means of distinguishing between the first and third of these classes of constituents, the proteids and related bodies on the one hand, and the simpler amides and amido-acids—sometimes grouped together as "nitrogenous extractives"—on the other. Incidentally only, some experiments have been made with representatives of the gelatinoid class.

Nutritive Values of Three Classes.

It is commonly assumed that proteids, gelatinoids, and the simpler amides have very different nutritive values, and, while all authorities would agree in assigning the highest value to the first of these, there is probably no small difference of opinion as to the order in which the second and third should be rated. In considering such a question, there should be separately taken into account relative digestibility or solubility, capability of undergoing osmotic absorption, and oxidisability in order to the production of energy. At present no definite numerical statement of the relative nutritive values of nitrogenous bodies of these three classes can be made. It seems much to be desired that more extended experiments than have so far been recorded should be made upon living animals—as far as possible upon human beings—in regard to the utilisation of both the gelatinoids and the simpler amides. The latter no doubt undergo oxidation to some extent in the animal body, and produce some energy in consequence. It is probably true of these simpler amidic substances that much larger quantities than analysis exhibits as constituents of the food consumed, or than analysis detects among the residua of food rejected from the body without having undergone complete oxidation, may be constantly formed among the earlier products of the metabolism of the proteids, and afterwards themselves undergo further change into the simpler and more stable forms of carbon dioxide, water, and urea.

Lack of Precision in Chemical Constitution.

It must be admitted that to a chemist the question of distinguishing between the proteids and the simpler

amides is not one of a scientifically precise character. The proteids doubtless contain at least a part of the nitrogen in the amidic relation, and where the line is to be drawn between more complex and more simple amides is, of course, more or less a matter to be arbitrarily decided. But of greater importance still is the doubt whether any of the so-called proteids are entitled to recognition as definite chemical substances. We usually understand by the term "a definite chemical substance" a substance of which all the molecules are exactly alike in constitution. Thus to the chemist the identity of such a substance as pure common salt, or cane sugar, or caffeine, depends on the absolute identity in character of all the myriad molecules of which even the smallest sensible mass is made up. But in regard to such materials as these we are able to determine the relative and absolute number of atoms of the elements of which each molecule is composed, and in many cases their order of attachment to each other, or the "structure" of the molecule. On the other hand, we have reason to believe that the so-called proteids are made up of molecules of such extreme complexity, assemblages of such large numbers—hundreds—of atoms of carbon, hydrogen, oxygen, and nitrogen, that we can make but random guesses at their arrangement, and cannot even determine with any certainty their number, relative or absolute. We talk of albumen, myosin, syntonin, as if these terms stood for pure chemical substances in the same sense that attaches to ammonia, benzene, or urea. But it is by no means certain that in a specimen of the most carefully prepared albumen from blood or white of egg any hundred, or any ten, molecules are absolutely alike. It may well be that a minute specimen of such a material consists in reality of numerous more or less similar, but yet in some respects different, molecules, which we lump together under a single name merely because they have a general resemblance, with certain properties in common. Furthermore, in nutrition investigations we have to deal with articles of food representing complex mixtures of substances referable to the two classes of the proteids and nitrogenous extractives, with many other things besides. Hence, an answer to the question to be examined must be a limited one, and such only as may serve the limited purpose of practical application in connection with nutrition investigations. Any process of separation, to be of value in such application, must be reasonably simple, and capable of being carried out without too great consumption of time.

List of Substances Examined.

A good deal of work was necessary at the outset in procuring satisfactory specimens of the several substances to be examined. Some of these have been prepared out and out in this laboratory from natural animal or vegetable sources. Some have been purchased in a more or less crude state and carefully purified. Some have been purchased and their purity ascertained by testing.

The following representatives of the simpler amidic and imidic compounds were experimented with:—

Amido-acids of the fatty series:—

- Glycocin (glycocoll or amido-acetic acid).
- Alanin (α -amido-propionic acid).
- Leucin (amido-caproic acid).

Amido-acids of the succinic acid and allied series:—

- Aspartic acid (amido-succinic acid).
- Asparagin.
- Glutamic acid (α -amido-oxyglutaric acid).
- Glutamin.

Amido-acid, including a benzene nucleus:—

- Tyrosin (oxy-phenyl- α -amido-propionic acid).

Betaine bases:—

- Betaine.

Guanidine bases:—

- Kreatin.
- Kreatinin.

Bases and neutral amides related to uric acids:—

- Hypoxanthine (sarkine).
- Carnine.
- Allantoine.

As representatives of the proteids and allied substances the following were used:—

- Albumen, from white of egg.
- Albumen, from blood.
- Fibrin, from blood.
- Casein, from milk.
- Legumin, from peas.
- Globulin (para-globulin), from serum of blood.
- Vitellin, from yolk of egg.
- Myosin, from muscular tissue.
- Syntonin (acid albumen), from muscular tissue).
- Hæmoglobin (mainly oxyhæmoglobin), from blood corpuscles.
- Albumose, from egg albumen.
- Peptone, from fibrin of blood.
- Gelatin, from skin.
- Chondrin, from cartilage.

Solutions used in Experiments.

These were, for the experiments by precipitation, brought into solution as follows, involving, as will be seen, change of chemical constitution in some cases:—

- Albumen, } dissolved in cold water.
- Hæmoglobin, }

- Gelatin, } dissolved in hot water.
- Chondrin, }

Fibrin, brought sparingly into solution by prolonged action of a 10 per cent solution of sodium chloride in water.

Fibrin, digested with a 4 per cent solution of caustic soda, and the solution afterwards acidified with acetic acid.

Casein, dissolved in 1 per cent solution of caustic soda, and the solution cautiously treated with dilute acetic acid to an extent just short of coagulation.

Globulin, dissolved in 5 per cent solution of sodium chloride.

Vitellin, } dissolved in 10 per cent solution of sodium
Myosin, } chloride.

Syntonin, dissolved in 0.1 per cent solution of hydrochloric acid.

Albumose, from the early stage of digestion of egg albumen by means of pepsin and 0.2 per cent solution of hydrochloric acid.

Peptone from advanced stage of digestion of blood fibrin by means of trypsin and 0.25 per cent solution of sodium carbonate.

Foods Involved in the Investigation.

While it was especially desirable to ascertain the behaviour of these several substances, of both classes, in their separate condition, it was borne in mind that in connection with nutrition investigations they have to be dealt with as constituents of ordinary food materials, principally the following:—

Meats, including poultry and fish (raw and cooked), soups and stews, meat extracts, eggs, milk and cheese, bread and other farinaceous preparations such as cakes and pastry, fruits and raw table vegetables, cooked fruits and table vegetables, fruit conserves, undigested and unabsorbed residues of food.

It was assumed as probable that the same method in detail would not be best adapted to all cases, but would be likely to need modification in application under different conditions.

Of course, the investigation undertaken has gone over ground already well trodden, and the results recorded by Schulze, Barbieri, Sachsse, Kormann, Boemer, Huefner, Allen, Tankard, Chittenden, Osborne, Wiley, and others, have been carefully examined.

The experimental work of the present investigation is reported, not altogether in the order in which it was done, but rather in logical succession, taking account first of physical differences, between the classes of substances to be distinguished, then of the effects of chemical agents of decomposition, and, lastly, of relations to solution and precipitation.

(To be continued).

CONTRIBUTION TO THE KNOWLEDGE OF THE RUTHENOCYANIDES.

By JAS. LEWIS HOWE.

POTASSIUM ruthenocyanide was described by Claus, in 1854, in his "Beiträge zur Chemie der Platinmetalle." The salt was formed by fusing ammonium rutheninitrosochloride (Joly, *Comptes Rendus*, 1889, cviii., 854; Howe, *J. Am. Chem. Soc.*, 1894, xvi., 388), tetrachloride of Claus, with potassium cyanide. The attempt was also made to form it by fusing potassium ferrocyanide with ruthenium, but it was found impossible to separate the ferrocyanide and ruthenocyanide. It is probable that some of Claus's experiments were carried out with a ruthenocyanide contaminated with ferrocyanide, from the fact that he describes copper ruthenocyanide as brown, whereas, when free from the ferrocyanide, it is pale green. Potassium ruthenocyanide in reactions and crystallisation resembles very closely the ferrocyanide, except that when pure it is white. Its crystallography as well as that of the isomorphous ferrocyanide and osmocyanide are described by A. Dufet (*Comptes Rendus*, 1895, cxx., 377).

Preparation of potassium ruthenocyanide for the purpose of carrying out experiments upon it not yet completed, gave occasion to the work recorded in this paper.

In the Claus method of preparation, a large proportion of the ammonium rutheninitrosochloride is decomposed with separation of metallic ruthenium, and while a part of the ruthenocyanide formed crystallises out from a solution of the melt, in large square pseudorhombic plates, much is left in the solution, and cannot be directly separated from the potassium cyanide and other salts present. Attempts were therefore made to use other methods of formation, with the following results:—

1. Potassium rutheninitrosochloride, K_2RuCl_5NO , fused with potassium cyanide, gave rather better results in ruthenocyanide, there being rather less decomposition than was the case with the ammonium salt.

2. Ruthenium trichloride, $RuCl_3$, fused with potassium cyanide, gave a fair product of ruthenocyanide.

3. Metallic ruthenium, fused with potassium cyanide, was slightly acted upon, giving a trace of ruthenocyanide.

4. Metallic ruthenium, fused with potassium cyanide and a little potassium hydroxide, gave rather stronger reaction than case 3, but the amount of ruthenocyanide formed was very small.

5. The melt formed by fusion of ruthenium in potassium hydroxide and nitrate, containing potassium ruthenate, K_2RuO_4 , was dissolved in water, and boiled with potassium cyanide. The deep orange-red solution was quickly decolourised, and the ruthenium was converted into ruthenocyanide with little loss. A considerable proportion could be obtained in the usual square crystals. This process could, by modification, probably be made the most satisfactory method of forming the ruthenocyanide, presenting one decided advantage that metallic ruthenium, or oxides, can be used, thus avoiding the necessity of preparing the nitrosochloride or chloride.

6. Ruthenium trichloride was boiled with a strong solution of potassium cyanide. The ruthenocyanide, crystallising in the usual square form, was obtained, but very much contaminated with a greenish by-product not yet investigated, probably analogous to Prussian blue.

7. Potassium rutheninitrosochloride was boiled with a strong solution of potassium cyanide. The solution was slowly decolourised, considerable of the greenish by-product being formed. From this solution there crystallised thick straw-coloured hexagonal plates, which will be considered further on. The quantity of the product is not satisfactory.

8. The Weselsky method (Weselsky, *Sitzber. Akad. Wien.*, 1870, lx., [2], 261; *Ber. d. Chem. Ges.*, 1869, ii., 588) of forming double cyanides was tried. Hydrocyanic acid was led into a solution of the nitrosochloride, in which barium carbonate was suspended until effervescence ceased. The solution gave no reaction for ruthenocyanide. Its colour had changed to the brown-yellow of the trichloride, but gave no reaction for this with potassium thiocyanate, or with ammonia and sodium thiosulphate. On warming, the solution gelatinised to a firm hydrogel, insoluble in hot aqua regia, but soluble in boiling potassium hydroxide. This last solution was unchanged on acidification with hydrochloric acid, and gave the potassium ferrocyanide reaction for nitrosochloride, but no reaction for trichloride. The dried jelly was easily explosive on heating. It presents an interesting analogy to Jackson's (*Ber. d. Chem. Ges.*, 1896, xxix., 1020) hydrogel of cobaltocyanide, and is being further studied.

9. The Weselsky method was also applied to ruthenium trichloride. The merest trace of ruthenocyanide was formed, and the solution, little changed in colour, no longer gave reactions for the trichloride.

10. The nitrosohydroxide of Joly, formed by the precipitation of the chloride by potassium carbonate, is easily soluble in potassium cyanide, and converted into ruthenocyanide by prolonged boiling.

The following reactions of ruthenocyanide may be noted:—

No precipitates are formed with the caustic alkaline earths, their ruthenocyanides being soluble in water.

Lead acetate gives a fine white precipitate, soluble in nitric acid.

Silver nitrate gives a white curdy precipitate, insoluble in both ammonia and in nitric acid.

Ferric chloride gives a rich purple precipitate, closely resembling Prussian blue in its chemical properties. In pure water it is soluble, but is precipitated from this solution by salts or alcohol. It forms a very beautiful and intense dye, adhering with great persistence to cotton fibre on which it has been precipitated. It is decomposed very readily by alkalis with precipitation of ferric hydroxide, re-forming, however, on the addition of acids, unaffected by dilute acids, but permanently decomposed by strong acids. It is a most delicate reaction for the detection of ruthenocyanide.

Ferrous sulphate gives a pale blue precipitate, which gradually changes to the purple above mentioned, and instantly if bromine water is added.

Copper sulphate gives a very pale green flocculent precipitate (not brown as given by Claus).

With salts of the following metals precipitates are formed insoluble in hydrochloric acid:—Cadmium, white (soluble in hot acid); zinc, white; tin (both stannous and stannic), white; mercury, white; bismuth, white (insoluble in nitric acid); nickel, dirty green (changing to blue with hydrochloric acid); cobalt, pale red; platinum, yellow-green; manganese gives a white precipitate soluble in hydrochloric acid. With gold there is no immediate precipitate, but a gradual darkening and separation of a dark precipitate, the solution becoming green.

Bromine water changes the solution to a dark red, which does not give the trivalent ruthenium reaction. Iodine also seems to alter the solution.

No reaction with hydrogen sulphide, ammonium sulphide, or thioacetic acid.

Nitric acid has no effect in the cold, but when heated slightly reddens the solutions. It then shows no signs of a reaction analogous to that of the nitroprussides.

	Theory for $\text{Ba}_2\text{Ru}(\text{CN})_6, 6\text{H}_2\text{O}$.	From RuCl_3 and KCN solution. I.	Found.					
			From RuCl_3NO by fusion.			From RuCl_3NO by solution.		
			II.	III.	IV.	V.	VI.	VII.
Barium	42.90	—	—	—	42.46	43.32	42.27	42.54
Ruthenium	15.86	16.41 (with SiO_2)	15.67	—	15.72	17.92 (with SiO_2)	15.80	15.60
$5\frac{1}{2}\text{H}_2\text{O}$ (100°)	15.67	15.67	15.63	—	15.68	—	—	15.53
$6\text{H}_2\text{O}$ (200°)	16.83	16.68	16.85	—	16.69	16.71	16.56	16.68
5C	9.37	—	—	—	—	—	—	—
6C	11.23	—	—	—	—	—	—	—
C from combustion	—	—	—	9.91	9.16	9.96	—	9.98
C in residue	—	—	—	2.65	2.03	—	—	2.30
Total carbon	—	—	—	12.56	11.19	—	—	12.28

It is acted on by potassium nitrite with sulphuric acid, and when neutralised gives a fugitive rose-red with ammonium sulphide.

It gives no apparent reaction with ruthenium trichloride or nitrosochloride.

Two methods of purification, applicable to such portions of the ruthenocyanides as cannot be separated by crystallisation, may be used. The most satisfactory is the precipitation in dilute solution by lead acetate and thorough washing with hot water to remove any lead chloride present. Suspension of the lead ruthenocyanide (carbonate, cyanide, &c.) in much water and decomposition with dilute sulphuric acid. Filtration and addition of baryta water till nearly neutral, and then of barium carbonate in excess; warming, filtration, and evaporation to crystallisation of the barium ruthenocyanide from which other ruthenocyanides may be formed by double decomposition.

The other method of purification which is applicable especially to all residues, is precipitation with ferric chloride in slightly acid solution, washing with acidified water, as far as possible (the purple begins to dissolve as the salts are washed out), and decomposing with baryta-water. This method, while very useful for recovery of residue, does not give so pure a product as the first method.

The hexagonal crystals described above, in Process 7, presented points of interest, in that it seemed not impossible that they contained the nitroso-group of the nitrosochloride from which they were formed. When dissolved in water they showed every reaction of the ordinary square crystals of the ruthenocyanide, but they could not be converted into the square form by re-crystallisation, nor could their yellowish tint be removed. The crystals are anhydrous, while the white crystals contain three molecules of water of crystallisation. On heating they explode with considerable violence, while the square crystals decompose very gently. On re-crystallisation they show prismatic forms, with many twins resembling staurolite crosses, and others resembling aragonite twins. Though perfectly hexagonal in form, they do not seem to belong to the hexagonal system. After conversion into the lead, hydrogen, barium, and back into the potassium salt by the first method of purification described, and further precipitation of this potassium salt by alcohol and re-crystallisation from water, crystals were obtained which were square, white, and in every respect—crystallographically as well as chemically—resembled the ordinary potassium ruthenocyanide. This was verified by analysis of the barium salt and partial analysis of the potassium salt.

It is evident that the hexagonal crystals are not a nitrosocyanide, and it seems possible that the form may be conditioned by some trace of impurity. They are being further studied at present.

Analysis of Potassium and Barium Ruthenocyanides.

Potassium Ruthenocyanide, $\text{K}_4\text{Ru}(\text{CN})_6, 3\text{H}_2\text{O}$, formed by boiling a solution of potassium rutheninitrosochloride with potassium cyanide; purified by conversion through lead, hydrogen, and barium salts.

	Per cent.
I. Loss of water in four days standing over sulphuric acid	10.84
II. Loss of water at 120°	10.90
III. Loss of water in thirty hours standing over sulphuric acid	11.25

Theory for $\text{K}_4\text{Ru}(\text{CN})_6, 3\text{H}_2\text{O}$.. $3\text{H}_2\text{O} = 11.53$

The crystals, especially when small, are so efflorescent that it is difficult to obtain uneffloresced salt for analysis, and the following are calculated for the dehydrated salt.

	Theory for $\text{K}_4\text{Ru}(\text{CN})_6$.	Found.		
		I.	II.	III.
Potassium	37.76	37.22	38.32	37.28
Ruthenium	24.53	23.90	24.22	24.44

This corresponds to the potassium ruthenocyanide described by Claus.

Barium Ruthenocyanide, $\text{Ba}_2\text{Ru}(\text{CN})_6, 6\text{H}_2\text{O}$ (new), formed from the ordinary form of the potassium salt.

Pale straw-coloured diamond-shaped (up to $\frac{1}{2}$ c.m. long) monoclinic crystals, or larger crystal rosettes, slightly soluble in cold, more easily in hot water, slowly lose water of crystallisation over sulphuric acid, lose $5\frac{1}{2}$ molecules of water at 100°, but retain $\frac{1}{2}$ molecule to nearly 200°, thus resembling barium ferrocyanide. The barium ruthenocyanide from the hexagonal form of the potassium salt was similar, but was not obtained in well enough defined crystals to identify positively with the preceding, but analysis shows the constitution to be the same.

The method of analysis was the following:—The salt was heated in a platinum boat (in two cases porcelain was used and attacked, so that the ruthenium was contaminated by silica—Analyses I. and V.) in an oxygen current, and the carbon dioxide evolved collected in an absorption apparatus. The proportion given off was variable, but usually a little more than 5 atoms. The boat was then heated in a hydrogen current, to reduce the oxide of ruthenium formed. The boat was then placed in a carbon dioxide apparatus and treated with hydrochloric acid, and the remainder of the carbon dioxide collected. The barium chloride was then filtered off from the ruthenium and determined as sulphate; the ruthenium, after burning the filter-paper and heating in a hydrogen current in a porcelain boat, was estimated as the metal. It was not found possible to arrive at any agreement in different analyses as to the loss on heating the barium salt in air, or oxygen, or subsequently in hydrogen. While most of the carbon of the cyanogen is burned to carbon dioxide, a part remains as barium carbonate. The remainder of the barium seems to fluctuate between oxide and peroxide, while a variable portion of the ruthenium is oxidised. The analyses show conclusively that six atoms of carbon are present in the salt derived from the nitrosochloride, hence one cyanogen group cannot be replaced by the nitroso-group.

The results of several analyses are given in the accompanying table.—*Journal of the American Chemical Society*, xviii., No. 11.

DETERMINATION OF CARBON IN IRON AND STEEL WITHOUT COMBUSTION APPARATUS.

By GEORGE T. DOUGHERTY, Chicago.

THERE has been a need of long standing for a reasonably quick and simple method of determining both kinds of carbon in iron and steel, with accuracy of results equalling the standard method of combustion in oxygen, or with sulphuric and chromic acids. Methods for estimating graphitic carbon, one among them by Eggertz, the father of the carbon colour test, are given in text-books; but all of them prescribe details or conditions which result in ruining their success for quick filtering or accurate work, and have been almost universally abandoned as giving too crude estimations. It is desirable to avoid gelatinising the silicon as much as possible, for silica freshly separated retains more or less hydrated water when dried at 100–115° C. Nitric acid diluted dissolves titanium carbide and other carbides, while dilute hydrochloric acid will not do quite as much, and usually leaves a dirty looking residue, which requires washing with caustic potassa, alcohol, and ether. The following method for graphite I have designed to overcome all difficulties or objections, and, judging by my own experience as proved by checks with irons containing known quantities of graphite, leaves very little to be desired for simplicity of operations and reliability of results.

Method for Graphite.

Dissolve 1 grm. of pig or cast iron drillings in 60 c.c. of nitric acid, 1.135 sp. gr. (the same acid as is used for rapid phosphorus work); heat gently until all are dissolved, and boil a few minutes to cook the combined carbon entirely into solution. Do not evaporate unduly, or use stronger acid, or much less acid of the specified strength, for more silicon would gelatinise and increase the insoluble residue. Have weighed previously a Gooch crucible, with its lid and cap, and put a disk of ashless filter-paper (about the area of a dime or penny) in the crucible and weigh again. Fit the Gooch crucible with the paper disk in it in the filtering bottle in connection with the filter pump in action, and pour water in to cause the paper to adhere perfectly to the bottom of the crucible. Now filter the solution of the iron, and wash five times with hot 10 per cent nitric acid, and once or twice with hot water. This operation of filtering and washing usually need not consume more than ten or fifteen minutes with good suction. Dry the crucible and contents to constant weight at 115–120° C. on the hot plate under a large inverted broken beaker with an opening in the top for a thermometer, which should touch the hot plate. This apparently crude air bath desiccates 100 to 200 per cent more quickly than the regulation copper air bath, probably because it allows of a constant current of air. The increase of weight (*a*) over the tare of the crucible and paper disk represents graphite and other insoluble residue. Burn off the graphite over a good Bunsen burner and weigh again when cool. The increase of weight over the tare of the crucible alone gives the amount (*b*) of siliceous residue. The difference between *a* and *b* indicates the quantity of graphite. The residue, which is silicon with sometimes a little iron oxide, usually amounts to from 0.0005 to 0.0040 grm., and the amount of hydrated water retained in the dried insoluble residue cannot on this small quantity of silica have amounted to anything to be allowed for in ascribing the entire loss on ignition to graphite. The graphite thus obtained burns off much more expeditiously than when it has been deposited on tared or counterpoised filters as used in the several old methods. Counterpoised or tared filters frequently give "shaky" results as in the determination of other elements. Paper disks (ashless), owing to their very small areas, are constant in weight, and are certain to filter more quickly than asbestos layers

in Gooch crucibles at all times. Besides, the asbestos filter is found to retard the burning of graphite, since you cannot by means of a platinum wire very well press the latter against the red-hot walls of the crucibles.

Two Methods for Combined Carbon.

1. The well-known colour method, which need not be described in detail here, may generally be applied with considerable safety if you know the previous history of irons to be tested, and have a standard iron of similar treatment whose carbon is not too widely different. White or mottled iron, for instance, cannot be reliably read off with a soft iron standard. Steel standards may be used, if they have been found by actual experiments to correspond well with various irons of known carbon contents. I have on hand such a steel standard (0.31 per cent carbon), which is, of course, more convenient to use than a standard pig or cast iron, since steel drillings are uniform in carbon, and do not require filtering when dissolved, while the whole lot of iron drillings must be mixed well on paper every time they are required, or segregation of graphite will ultimately occur with disastrous consequences. I do not, however, attempt to use that steel standard with irons of high combined carbon; in a case of recent occurrence it would show 2.64 per cent of combined carbon in a sample of white iron which had actually 2.49 per cent. The colour method is, therefore, of limited value unless performed under certain conditions, and these conditions must be religiously adhered to. When the carbon in a sample of iron or steel is so low that its solution appears greenish instead of brownish when read in the camera behind the usual ground glass in daylight, or when artificial light is required, a thin slab of porcelain (such as they make lamp shades of) in the place of ground glass before an electric light will be found to remove entirely the green shade of low carbon tests, and bring out different tints of brown colour quite sharply and unmistakably.

2. The alternate method, which is more universal in application, and, like the one given above for graphite, aspires to equal the "old reliable" combustion process, is similar in some of the operations to the graphite method, and is as follows:—

Pour on 1 or 2 grms. of drillings in a dry beaker 60 or 100 c.c. of a slightly warm 33 per cent solution of double chlorides of copper and potassium, acidulated with 5 per cent of strong hydrochloric acid. Frequent or continual stirring greatly promotes the solution of the copper thus displaced. As for graphite, weigh the Gooch crucible alone, and again with a paper disk in it. Turn on suction, pour water on, and then the copper and iron solution, wash twice with hot dilute hydrochloric acid (1 acid to 3 water), twice with hot water, four times with hot nitric acid of 1.135 sp. gr. (this to dissolve out copper sulphide and any particle of metallic copper), and finally twice with hot water. Dry to constant weight at not exceeding 120° C. on the hot plate, taking more care regarding temperature than is necessary for graphite. The increase of weight over that of the crucible and paper disk represents the quantity (*a*) of graphite, organic compound, and insoluble siliceous residue, with often a little copper oxide. Burn off the graphite and organic compound and weigh again. The amount (*b*) of residue after ignition is shown by the increase of weight over the tare of the crucible alone. Deduct *b* from *a*, and the remainder (*c*) is graphite plus organic compound. Again deduct from *c* the amount of graphite elsewhere determined; the remainder (*d*) is organic compound, which multiplied by 0.675 gives the amount of combined carbon. This method seems to be fully equal to the elaborate standard combustion process, and has the advantage of being simpler and quicker, with fewer possible sources of error. Some time ago I happened to find out that combined carbon set free by the double chloride of copper and potassium did not deposit in the form of pure carbon as commonly supposed, but of an organic compound of unknown composition, and I pro-

ceeded to standardise its actual percentage of carbon, which was done by treating by the method just described three steel standards of different carbons, which I had on hand, namely, 0.17, 0.31, and 0.48 per cent. The average of the results obtained, which, by the way, were pretty close, gave 67.50 per cent of carbon, which I have adopted as the factor on the organic compound, which is certainly deserving of further study. If an asbestos filter be used instead of a paper disk it would require a factor rather lower, but does not give equally satisfactory or uniform results.

It may prove interesting by way of illustration and comparison to subjoin the results of a recent analysis of standardised cast iron drillings marked A, and furnished by the Standardising Bureau of the American Foundrymen's Association, whose official figures for that sample are 3.11 per cent graphite and 0.56 per cent combined carbon, the average of combustion determination by four different parties:—

1 grm. taken for graphite.

	Grms.		Grms.
Crucible =	14.0263	Crucible + disk = ..	14.0682
	14.0255		14.0362
Residue after igni- tion =	0.0008	Total matter on drying =	0.0320
		Residue after igni- tion =	0.0008
		Loss by ignition =	0.0312
		$0.0312 \times \frac{1.00}{1.1} = 3.12\%$	graphite.

1 grm. taken for combined carbon.

	Grms.		Grms.
Crucible =	14.0268	Crucible + disk = ..	14.0820
	14.0252		14.0415
Residue after igni- tion =	0.0016	Total matter on drying =	0.0405
		Residue after igni- tion =	0.0016
		Loss by ignition =	0.0389
		Graphite =	0.0312
		Organic compound =	0.0077
		$0.0077 \times 0.675 \times \frac{1.00}{1.1} = 0.52\%$	combined carbon.
By colour with 0.31 % carbon		0.51 % combined carbon.	
steel standard		0.52 % combined carbon.	

Before concluding this article it will be important to point out that the last method given above is not applicable to ferromanganese without considerable modification in the details of the operation and in the factor used for calculation. Copper is an elementary constituent of the organic compound containing the carbon of ferromanganese separated by potassio copper chloride; and it would be unsafe to use a platinum Gooch crucible with a paper disk for estimating it, since copper would be reduced from its combination and attack the bottom of the crucible, as it has done in my experience. In such a case, unless one has an arrangement for passing oxygen gas into the crucible during the ignition, an asbestos layer may be used in lieu of a paper disk. Instead of 0.675 as for iron and steel, the factor would be 0.80 or more, depending largely on the mode of operation. I purpose to investigate and work out more fully this point later.—*The Iron Age*.

Reducing Properties of Boron and of Aluminium.—MM. Duboin and Gauthier.—If boron and silicon are mixed intimately with alumina in a porcelain tube, the whole then raised to a very high temperature and a current of chlorine passed along the tube for some time, chloride of aluminium and boric acid are formed.—*Comptes Rendus*, cxxix., No. 4.

NOTICES OF BOOKS.

Die Aetherischen Oele. Von E. GILDEMEISTER und FR. HOFFMANN. Bearbeitet im Auftrage der Firma Schimmel und Co., in Leipzig. Berlin: Verlag von Julius Springer. 1899. Pp. iv., [ii.], 919. Roy. 8vo. Ill.

THIS monumental work forms a practical and scientific encyclopædia on essential oils in all their bearings, botanically, chemically, and commercially; it is divided into three main parts—a historical introduction of 95 pages; a general treatise on the theoretical extraction, the occurrence, and valuation of essential oils (in 185 pages); and a special part which gives the history, origin, extraction, properties, composition, valuation, and statistics of each of 422 oils.

In the preparation of this comprehensive work, the firm of Schimmel and Co. secured the services of several competent authors: Dr. Friedrich Hoffmann, many years resident in New York City, but now of Berlin, wrote the historical introduction, the history of the raw materials furnishing the oils, and the account of the American products; for the balance of the work Dr. Edward Gildemeister is responsible, with the exception of two chapters by Dr. C. von Rechenberg and by Dr. J. Helle.

The handsomely printed volume shows thoughtful care throughout; the typography and heavy paper leave nothing to be desired; the illustrations are excellent, notably the full-page pictures of modern distilling apparatus at pages 129–136. Two admirable maps—one showing the avenues of commerce in the Middle Ages, and one of Sicily showing the region of cultivation of oranges and lemons—are good features. Another excellent feature are the very numerous references to literature as footnotes, that constitute a veritable bibliography.

The historical introduction by Dr. Hoffmann shows deep research; it is agreeably illustrated by facsimiles from early woodcuts of quaint appearance.

The special part contains a mass of information not easily found elsewhere, and makes an invaluable work of reference for those interested in the subject.

A good index closes the handsome volume.

H. C. B.

The Analysis of Minerals. (Traité d'Analyse des substances minerales). By A. CARNOT. Membre de l'Institut, Inspecteur-general of Mines, &c. Vol. I. Paris: Vve. Ch. Dunod. 1898. Pp. 992.

THIS magnificent work, of which the first volume is now before us, has been written with the idea of making known the present state and the applications of mineral chemistry. The author has devoted himself to this subject for over thirty years, and during this time has examined all kinds of minerals, rocks, metals, mineral waters, &c. In the present volume he has arranged and co-ordinated the large number of documents which have accumulated during this long period, in the hope that his experience will be of profit to young chemists.

About one half of the volume is devoted to qualitative researches, and the remainder to general operations of quantitative analysis, the details of which will fill two more volumes to follow.

The early chapters deal with examination by the dry way, blowpipe analysis, spectroscopic methods, micro-chemical examination, &c., followed by the methods of the wet way. The author has devised a new system by means of which not only the commoner elements can be detected in very complex mixtures, but also the numerous so-called rare earths which modern progress in chemistry no longer allows us to pass over. This important subject commences on page 201, and continues to page 296. This is followed by a chapter on the principal characteristics of the bases and acids corresponding to the different elements, and a chapter on the preparation and use of reagents, and their purification.

The second part commences with instructions as to taking samples of materials often very heterogeneous in character; numerous details are given on means of heating, forms of apparatus to be used, and precautions to be taken for preventing causes of error in the weighing of bodies, &c.

Special chapters are devoted to electrolytic methods, volumetric analysis by saturation, oxidation, reduction, precipitation, and colorimetry.

The last chapter deals with the qualitative and quantitative analysis of gas, and of gaseous mixtures.

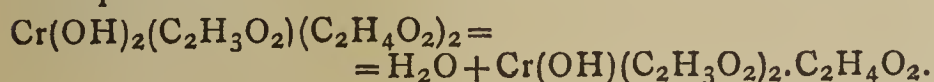
We have no doubt that this volume will be highly appreciated by all chemists, old and young, and we congratulate the author on its production.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

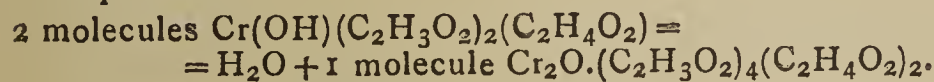
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 5, July 31, 1899.

Isomeric Forms of Chromic Acetate.—A. Recoura.—In a recent paper the author describes two of the isomeric forms of chromic acetate. The present communication contains an account of the preparation and properties of the remaining two forms—(1) A second violet acetate, or chromo-mono-acetic acid, with formula $\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_3\text{H}_2\text{O}$, a substance which in the solid state and in solution is a violet colour. It is not a true chromium salt, but a monobasic acid. It is produced by the spontaneous transformation of the dibasic acid, which takes about ten days. The reaction can be expressed by the equation—



(2) Green chromo-mono-acetic acid, with formula $\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_3.\frac{1}{2}\text{H}_2\text{O}$, is green both in the solid state and in solution. It possesses properties very similar to those of the violet acid. It is produced by the spontaneous transformation of the solution of the violet acid. The action is very slow, probably taking a year, but is rendered very rapid by boiling the solution of the violet acid with acetic acid. The reaction may be expressed by the equation—



Action of Magnesium on Saline Solutions.—Georges Lemoine.—Magnesium decomposes water very slowly at ordinary temperatures, but in the presence of certain salts, and with the magnesium in the form of powder, the action becomes very lively. Taking, for example, the chloride, the following action probably takes place:— $\text{MgCl}_2 + m\text{Mg} + m\text{H}_2\text{O} = \text{MgCl}_2 + m\text{H}_2 + m\text{MgO}$. The author has measured the gas evolved after varying times, and has studied this reaction thermochemically.

Dissociation of Hexammoniacal Cadmium Chloride.—W. R. Lang and A. Rigaut.—The authors have investigated the dissociation of combinations of ammonia with anhydrous cadmium chloride, using liquefied ammonia-gas and powdered cadmium chloride. They determined the tensions of dissociation of hexammoniacal cadmium chloride, and found that above 62° the compound $\text{CdCl}_2.6\text{NH}_3$ cannot exist.

Dissociation of Mercury Diammonium Iodide.—Maurice François.—Ammoniacal mercuric iodide does not behave in the same manner as ammoniacal silver chloride; its dissociation shows the existence of a white intermediate compound. During the first period of dissociation, $\text{HgI}_2.2\text{NH}_3$ decomposes into ammonia gas and

into the compound $3\text{HgI}_2.4\text{NH}_3$ without the production of mercuric iodide. This decomposition is characterised by a strong dissociation tension. During the second period, the compound $3\text{HgI}_2.4\text{NH}_3$ is decomposed into mercuric iodide and ammonia; the dissociation tension being very slight.

Action of Sodammonium and Potassammonium on Selenium.—C. Hugot.—The selenides of sodium and potassium, obtained by the action of sodammonium and potassammonium on selenium, present properties almost identical. The two salts correspond to the formulæ Na_2Se_4 and K_2Se_4 . This method of their preparation gives the compounds in a very high state of purity.

Some Acetylacetonates.—G. Urbain and A. Debiere.—The authors describe the preparation and properties of acetylacetonates of iron, manganese, cobalt, chromium, aluminium, and nickel. A comparison of the properties of these compounds shows the analogy between the sesquioxides of cobalt and manganese, and those of aluminium, iron, and chromium. Not only in all the acetylacetonates of the sesquioxides is the metal trivalent, but the physical and chemical properties are nearly identical. Their crystalline forms are also analogous; they melt without decomposition, and are all more or less volatile. They all combine with two molecules of chloroform when crystallised from this solvent.

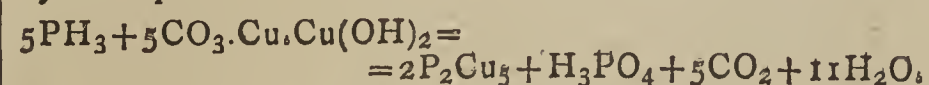
No. 6, August 7, 1899.

Thermo-chemical Determinations. Ethylenediamine.—M. Berthelot.—The present paper contains some determinations, following on those already published, for the investigation of the principles which underlie the production of animal heat and chemico-biological syntheses. These were carried out on the acids of bile, amygdaline (a very widely distributed glucoside in vegetable fruits, and which produces hydrocyanic acid and the essence of bitter almonds), conicine (the acid of hemlock), and, finally, ethylenediamine (the most simple type of bivalent alkaloids containing more than one nitrogen atom, which play so important a part among the therapeutic alkalis).

Ammoniacal Nitrate of Silver.—MM. Berthelot and Delépine.—The employment of ammoniacal nitrate of silver in certain calorimetric measurements, led the authors to make a complete study of this compound, which represents in reality the nitrate of a complex stable ammoniated base, forming two stable salts in solution. The base is as powerful as the mineral alkalis.

Action of Chlorine on a Mixture of Silicon, Silica, and Alumina.—Emile Vigouroux.—A mixture of silica and aluminium can be used to prepare chloride of silicon. This preparation takes place in two stages—(1) The reduction at a red heat of the silica by aluminium and the exhaustion by acids of the powder obtained. (2) The attack of the residue, when completely freed from acid, by chlorine.

Action of Phosphoretted Hydrogen on the Oxide, Hydrate, and Carbonate of Copper.—E. Rubenovitch.—Hydrogen phosphide attacks copper oxide immediately, at first slowly, then more energetically, a considerable quantity of heat being evolved. In the case of the hydrate, the action is so violent that the substance is rendered incandescent. To moderate the reaction, the gas must be admitted into the presence of the hydrate in small quantities at a time. The carbonate used in this experiment is the one obtained by precipitating copper sulphate with carbonate of soda, $\text{CO}_3.\text{Cu}.\text{Cu}(\text{OH})_2.5\text{H}_2\text{O}$. The action of hydrogen phosphide on this substance is represented by the equation—



The phosphide obtained is greyish black, amorphous, and very soluble in nitric acid and bromine water.

Some Properties of Dioxycetone in Relation to the Degree of Molecular Aggregation. — Gabriel Bertrand.—Dioxycetone can exist in two forms, each having distinct properties and a different molecular state of aggregation. The study of these forms, and the conditions under which they pass from one to the other, permits of an explanation of certain physical anomalies of dioxycetone, such as superfusion and supersaturation.

MISCELLANEOUS.

Schools of Chemistry, &c.—The following information was received too late for insertion in the "Students' Number":—

NORTHERN POLYTECHNIC INSTITUTE, Holloway Road, N.—Head of Chemical Department: The Principal, J. T. Dunn, D.Sc.; Assistant Lecturers, Mr. H. Charles L. Bloxam, and Mr. W. H. Watson, A.R.C.S.; Secretary, Mr. E. Griffiths. Session begins September 25th. Evening Classes in Practical and Theoretical Inorganic and Organic Chemistry, 6 to 9.30 p.m., open to Students of either sex. The courses at present arranged extend over a period of four years. Instruction is also given in Elementary Chemistry applied to the Arts and Manufactures. A special course of demonstrations will be given on the theory and principles of Chemical Analysis. There is a special laboratory for Gas Analysis, and every facility is given for the prosecution of research. The Physical Department is under the charge of Mr. Victor A. Mundella, B.A., B.Sc. Besides the usual courses in Physics, an introductory course on Elementary Experimental Science (Mechanics, Physics, and Chemistry) is given conjointly by the Principal and Mr. Mundella.

STOCKPORT TECHNICAL SCHOOL.—Department of Chemistry and Dyeing.—Principal: Mr. R. J. Brown, M.Sc. A syllabus with full particulars of the courses of instruction, hours, fees, &c., is obtainable on application. Special instruction is given in the Dyeing of Felt, &c., as applied to Hat Manufacture.

QUEEN'S COLLEGE, BELFAST.—The Session commences on Tuesday, October 17th, 1899.

Institute of Chemistry of Great Britain and Ireland. July-August Examinations, 1899. — *Names of Candidates who passed the Intermediate Examination*:—A. W. Comber, Finsbury Technical College, London; J. Cooper, B.Sc. (Durham), Durham College of Science, Newcastle-on-Tyne; L. Eynon, Finsbury Technical College, London; W. Eyre, University College, Sheffield; J. Fotheringham, Glasgow and West of Scotland Technical College; W. A. Fyffe, University College, Dundee; H. Hall, University College, Nottingham; W. H. Jollyman, Finsbury Technical College, London; A. G. Levy, Finsbury Technical College, London; J. A. Lloyd, Mason University College, Birmingham; S. E. Melling, Owens College, Manchester, and under A. H. Allen, Esq., F.I.C.; W. G. Orme, Mason University College, Birmingham; C. J. Silverston, B.Sc. (Lond.), Mason University College, Birmingham; W. H. Taylor, Finsbury Technical College, London; V. W. Theobalds, Finsbury Technical College, London; H. L. Wall, Finsbury Technical College and University College, London. *Names of Candidates who passed the Practical Examination for the Associateship*.—P. Auchinachie (for Fellowship), under Cecil H. Cribb, Esq., F.I.C.; W. B. Clark, Glasgow and West of Scotland Technical College, and under J. Hornby, Esq. F.I.C.; C. R. Darling, Royal College of Science, Dublin; R. N. S. Doresa, Merchant Venturers' Technical College, Bristol, and under Dr. E. H. Cook, F.I.C.; E. Goulding, B.Sc. (Lond.), Registered Student under Professor W. R. Dunstan, M.A., F.R.S., F.I.C.; J. Kerr, B.Sc. (Edin.), Registered Student under Dr. Stevenson Macadam, F.I.C. *Names of Candidates who passed the Final Examination*

for the Associateship.—In Branch "A" (Mineral Chemistry: W. S. Denham, Glasgow and West of Scotland Technical College; E. R. Nind, A.C.G.I., City and Guilds of London Central Institution; J. G. A. Rhodin (for Fellowship), University of Upsala, Sweden, and under J. Wilson Swan, Esq., F.R.S., F.I.C.; J. H. Smith, Assoc. R.C.Sc. (Lond.), Royal College of Science, London. In Branch "B" (Metallurgical Chemistry): J. P. de Castro, B.A. (Cantab.), Cambridge University, and under Sir William Roberts-Austen, K.C.B., F.R.S.; W. T. Collis, Mason University College, Birmingham. In Branch "D" (Organic Chemistry): R. D. Abell, University College of North Wales, Bangor; W. A. Cates, Finsbury Technical College, London; R. L. Jenks, A.C.G.I., City and Guilds of London Central Institution.

NORTHERN POLYTECHNIC INSTITUTE, HOLLOWAY ROAD, N.

Principal and Head of Chemical Department—J. T. DUNN, D.Sc.
Assistants—H. CHAS. L. BLOXAM, W. H. WATSON, A.R.C.S.

SESSION begins **SEPT. 25th**. Evening Classes in **INORGANIC** and **ORGANIC CHEMISTRY**, Lectures and Laboratory Work. Courses are suitable for the Examinations of the Science and Art Department, and for those of the University of London for Degrees in Science. Facilities for Special Work and Research of Advanced Students. All details in Prospectus, obtainable at the Institute.

E. GRIFFITHS, Secretary.

GOLDSMITHS' INSTITUTE, NEW CROSS, S.E.

DEPARTMENT OF CHEMISTRY.

EVENING CLASSES, providing complete Courses of Instruction in various branches of Pure and Applied CHEMISTRY, are held at this Institute under the direction of Mr. WILLIAM JACKSON POPE, F.I.C., &c. The Courses of Lectures and Practical Laboratory teaching are suitable for Students desiring to qualify in Chemistry at the Examinations of the London University, the Pharmaceutical Society, the Science and Art Department, and other public bodies. The equipment of the Chemical Laboratories has been recently considerably augmented and exceptional facilities are offered to advanced Students who desire to engage in Chemical Research Work during the Day or Evening. The new **SESSION** commences on **SEPTEMBER 25th**. For further particulars apply to the Secretary.

J. T. REDMAYNE, B.A., Secretary.

THE DURHAM COLLEGE OF SCIENCE, NEWCASTLE-ON-TYNE.

JOHNSTON CHEMICAL SCHOLARSHIP.

This Scholarship (£60), tenable for one year, together with a PRIZE in Books to the value of £5, will be awarded on the result of an Examination in Chemistry with Crystallography or Mineralogy, to be held on September 27th and 28th. Candidates, who must be Bachelors in Science of a British University of not more than three years' standing, are required to send in their names ON OR BEFORE THE 23RD INST. to the Secretary, from whom further particulars may be obtained.

ROYAL TECHNICAL INSTITUTE, SALFORD.

Principal—W. WILSON, M.A.

The **NEXT SESSION** will **OPEN** on **SEPTEMBER 12th, 1899**.

Full Day Courses and Evening Classes in various subjects, including CHEMISTRY and DYEING and CALICO-PRINTING. Dye-house contains Jigs and Plant for Experimental Dyeing of full-width Calico, and in the Calico-printing Laboratory there is a complete range of full-sized Machinery.

Prospectus and particulars free upon application.

RICHARD MARTIN, Secretary.

THE CHEMICAL NEWS.

VOL. LXXX., No. 2077.

BRITISH ASSOCIATION

FOR THE

ADVANCEMENT OF SCIENCE.

DOVER, 1899.

INAUGURAL ADDRESS OF THE PRESIDENT,
PROF. SIR MICHAEL FOSTER, K.C.B., SEC.R.S.

HE who until a few minutes ago was your President said somewhere at the meeting at Bristol, and said with truth, that among the qualifications needed for the high honour of Presidency of the British Association for the Advancement of Science, that of being old was becoming more and more dominant. He who is now attempting to speak to you feels that he is rapidly earning that distinction. But the Association itself is older than its President; it has seen pass away the men who, wise in their generation, met at York on September 27, 1831, to found it; it has seen other great men who in bygone years served it as Presidents, or otherwise helped it on, sink one after another into the grave. Each year, indeed, when it plants its flag as a signal of its yearly meeting, that flag floats half-mast high in token of the great losses which the passing year has brought. This year is no exception; the losses, indeed, are perhaps unwontedly heavy. I will not attempt to call over the sad roll-call: but I must say a word about one who was above most others a faithful and zealous friend of the Association. Sir Douglas Galton joined the Association in 1860. From 1871 to 1895, as one of the General Secretaries, he bore, and bore to the great good of the Association, a large share of the burden of the Association's work. How great that share was is perhaps especially known to the many men, among whom I am proud to count myself, who during his long term of office served in succession with him as brother General Secretary. In 1895, at Ipswich, he left the post of General Secretary, but only to become President. So long and so constantly did he labour for the good of the Association that he seemed to be an integral part of it, and meeting as we do to-day, and as we henceforward must do, without Douglas Galton, we feel something greatly missing. This year, perhaps even more than in other years, we could have wished him to be among us; for to-day the Association may look with joy, not un-mixed with pride, on the realisation of a project in forwarding which it has had a conspicuous share, on the commencement of an undertaking which is not only a great thing in itself, but which, we trust, is the beginning of still greater things to come. And the share which the Association has had in this was largely Sir Douglas Galton's doing. In his Address as President of Section A, at the meeting of the Association at Cardiff in 1891, Professor Oliver Lodge expounded with pregnant words how urgently, not pure science only, but industry and the constructive arts—for the interests of these are ever at bottom the same—needed the aid of some national establishment for the prosecution of prolonged and costly physical researches, which private enterprise could carry out in a lame fashion only, if at all. Lodge's words found an echo in many men's minds; but the response was for a long while in men's minds only. In 1895 Sir Douglas Galton, having previously made a personal study of an institution analogous to the one desired—namely, the Reichsanstalt at Berlin—seized the opportunity offered to him as President of the Association at Ipswich to insist,

with the authority not only of the head for the time being of a great scientific body, but also of one who himself knew the ways and wants at once of science and of practical life, that the thing which Lodge and others had hoped for was a thing which could be done, and ought to be done at once. And now to-day we can say it has been done. The National Physical Laboratory has been founded. The Address at Ipswich marked the beginning of an organised effort which has at last been crowned with success. A feeling of sadness cannot but come over us when we think that Sir Douglas Galton was not spared to see the formal completion of the scheme whose birth he did so much to help, and which, to his last days, he aided in more ways than one. It is the old story—the good which men do lives after them.

Still older than the Association is this nineteenth century, now swiftly drawing to its close. Though the century itself has yet some sixteen months to run, this is the last meeting of the British Association which will use the numbers eighteen hundred to mark its date.

The eyes of the young look ever forward; they take little heed of the short though ever-lengthening fragment of life which lies behind them; they are wholly bent on that which is to come. The eyes of the aged turn wistfully again and again to the past; as the old glide down the inevitable slope their present becomes a living over again the life which has gone before, and the future takes on the shape of a brief lengthening of the past. May I this evening venture to give rein to the impulses of advancing years? May I, at this last meeting of the Association in the eighteen hundreds, dare to dwell for a while upon the past, and to call to mind a few of the changes which have taken place in the world since those autumn days in which men were saying to each other that the last of the seventeen hundreds was drawing towards its end?

Dover in the year of our Lord seventeen hundred and ninety-nine was in many ways unlike the Dover of to-day. On moonless nights men groped their way in its narrow streets by the help of swinging lanterns and smoky torches, for no lamps lit the ways. By day the light of the sun struggled into the houses through narrow panes of blurred glass. Though the town then, as now, was one of the chief portals to and from the countries beyond the seas, the means of travel were scanty and dear, available for the most part to the rich alone, and, for all, beset with discomfort and risk. Slow and uncertain was the carriage of goods, and the news of the world outside came to the town—though it from its position learnt more than most towns—tardily, fitfully, and often falsely. The people of Dover sat then much in dimness, if not in darkness, and lived in large measure on themselves. They who study the phenomena of living beings tell us that light is the great stimulus of life, and that the fullness of the life of a being or of any of its members may be measured by the variety, the swiftness, and the certainty of the means by which it is in touch with its surroundings. Judged from this standpoint life at Dover then, as indeed elsewhere, must have fallen far short of the life of to-day.

The same study of living beings, however, teaches us that while from one point of view the environment seems to mould the organism, from another point the organism seems to be master of its environment. Going behind the change of circumstances, we may raise the question, the old question, Was life in its essence worth more than now? Has there been a real advance?

Let me at once relieve your minds by saying that I propose to leave this question in the main unanswered. It may be, or it may not be, that man's grasp of the beautiful and of the good, if not looser, is not firmer than it was a hundred years ago. It may be, or it may not be, that man is no nearer to absolute truth, to seeing things as they really are, than he was then. I will merely ask you to consider with me for a few minutes how far, and in what ways, man's laying hold of that aspect of or part of

truth which we call natural knowledge, or sometimes science, differed in 1799 from what it is to-day, and whether that change must not be accounted a real advance, a real improvement in man.

I do not propose to weary you by what in my hands would be the rash effort of attempting a survey of all the scientific results of the nineteenth century. It will be enough if for a little while I dwell on some few of the salient features distinguishing the way in which we now-a-days look upon, and during the coming week shall speak of, the works of Nature around us—though those works themselves, save for the slight shifting involved in a secular change, remain exactly the same—from the way in which they were looked upon and might have been spoken of at a gathering of philosophers at Dover in 1799. And I ask your leave to do so.

In the philosophy of the ancients, earth, fire, air, and water were called "the elements." It was thought, and rightly thought, that a knowledge of them and of their attributes was a necessary basis of a knowledge of the ways of Nature. Translated into modern language, a knowledge of these "elements" of old means a knowledge of the composition of the atmosphere, of water, and of all the other things which we call matter, as well as a knowledge of the general properties of gases, liquids, and solids, and of the nature and effects of combustion. Of all these things our knowledge to-day is large and exact, and, though ever enlarging, in some respects complete. When did that knowledge begin to become exact?

To-day the children in our schools know that the air which wraps round the globe is not a single thing, but is made up of two things, oxygen and nitrogen,* mingled together. They know, again, that water is not a single thing, but the product of two things, oxygen and hydrogen, joined together. They know that when the air makes the fire burn and gives the animal life, it is the oxygen in it which does the work. They know that all round them things are undergoing that union with oxygen which we call oxidation, and that oxidation is the ordinary source of heat and light. Let me ask you to picture to yourselves what confusion there would be to-morrow, not only in the discussions at the sectional meetings of our Association, but in the world at large, if it should happen that in the coming night some destroying touch should wither up certain tender structures in all our brains, and wipe out from our memories all traces of the ideas which cluster in our minds around the verbal tokens, oxygen and oxidation. How could any of us, not the so-called man of science alone, but even the man of business and the man of pleasure, go about his ways lacking those ideas? Yet those ideas were in 1799 lacking to all but a few.

Although in the third quarter of the seventeenth century the light of truth about oxidation and combustion had flashed out in the writings of John Mayow; it came as a flash only, and died away as soon as it had come. For the rest of that century, and for the greater part of the next, philosophers stumbled about in darkness, misled for the most of the time by the phantom conception which they called phlogiston. It was not until the end of the third quarter of the eighteenth century that the new light, which has burned steadily ever since, lit up the minds of the men of science. The light came at nearly the same time from England and from France. Rounding off the sharp corners of controversy, and joining, as we may fitly do to-day, the two countries as twin bearers of a common crown, we may say that we owe the truth to Cavendish, to Lavoisier, and Priestley. If it was Priestley who was the first to demonstrate the existence of what we now call oxygen, it is to Lavoisier we owe the true conception of the nature of oxidation and the clear exposition of the full meaning of Priestley's discovery, while the knowledge of the composition of

water, the necessary complement of the knowledge of oxygen, came to us through Cavendish, and, we may perhaps add, through Watt.

The date of Priestley's discovery of oxygen is 1774, Lavoisier's classic memoir "On the Nature of the Principle which enters into Combination with Metals during Calcination" appeared in 1775, and Cavendish's paper "On the Composition of Water" did not see the light until 1784.

During the last quarter of the Eighteenth Century this new idea of oxygen and oxidation was struggling into existence. How new was the idea is illustrated by the fact that Lavoisier himself at first spoke of that which he was afterwards, namely in 1778, led to call oxygen, the name by which it has since been known, as "the principle which enters into combination." What difficulties its acceptance met with is illustrated by the fact that Priestley himself refused to the end of his life to grasp the true bearings of the discovery which he had made. In the year 1799 the knowledge of oxygen, of the nature of water and of air, and indeed the true conception of chemical composition and chemical change, was hardly more than beginning to be, and the century had to pass wholly away before the next great chemical idea, which we know by the name of the Atomic Theory of John Dalton, was made known. We have only to read the scientific literature of the time to recognise that a truth which is now not only woven as a master-thread into all our scientific conceptions, but even enters largely into the everyday talk and thoughts of educated people, was a hundred years ago struggling into existence among the philosophers themselves. It was all but absolutely unknown to the large world outside those select few.

If there be one word of science which is writ large on the life of the present time, it is the word "electricity"; it is, I take it, writ larger than any other word. The knowledge which it denotes has carried its practical results far and wide into our daily life, while the theoretical conceptions which it signifies pierce deep into the nature of things. We are to-day proud, and justly proud, both of the material triumphs and of the intellectual gains which it has brought us, and we are full of even larger hopes of it in the future.

At what time did this bright child of the Nineteenth Century have its birth?

He who listened to the small group of philosophers of Dover, who in 1799 might have discoursed of natural knowledge, would perhaps have heard much of electric machines, of electric sparks, of electric fluid, and even of positive and negative electricity; for frictional electricity had long been known and even carefully studied. Probably one or more of the group, dwelling on the observations which Galvani, an Italian, had made known some twenty years before, developed views on the connection of electricity with the phenomena of living bodies. Possibly one of them was exciting the rest by telling how he had just heard that a professor at Pavia, one Volta, had discovered that electricity could be produced not only by rubbing together particular bodies, but by the simple contact of two metals, and had thereby explained Galvani's remarkable results. For, indeed, as we shall hear from Professor Fleming, it was in that very year, 1799, that electricity as we now know it took its birth. It was then that Volta brought to light the apparently simple truths out of which so much has sprung. The world, it is true, had to wait for yet some twenty years before both the practical and the theoretic worth of Volta's discovery became truly pregnant, under the fertilising influence of another discovery. The loadstone and magnetic virtues had, like the electrifying power of rubbed amber, long been an old story. But, save for the compass, not much had come from it. And even Volta's discovery might have long remained relatively barren had it been left to itself. When, however, in 1819, Oersted made known his remarkable observations on the relations of electricity to magnetism,

* Some may already know that there is at least a third thing, argon.

he made the contact needed for the flow of a new current of ideas. And it is perhaps not too much to say that those ideas, developing during the years of the rest of the century with an ever-accelerating swiftness, have wholly changed man's material relations to the circumstances of life, and at the same time carried him far in his knowledge of the nature of things.

Of all the various branches of science, none perhaps is to-day, none for these many years past has been, so well known to, even if not understood by, most people as that of geology. Its practical lessons have brought wealth to many; its fairy tales have brought delight to more; and round it hovers the charm of danger, for the conclusions to which it leads touch on the nature of man's beginning.

In 1799, the science of geology, as we now know it, was struggling into birth. There had been from of old cosmogonies, theories as to how the world had taken shape out of primæval chaos. In that fresh spirit which marked the zealous search after natural knowledge pursued in the middle and latter part of the Seventeenth Century, the brilliant Stenson, in Italy, and Hooke, in our own country, had laid hold of some of the problems presented by fossil remains, and Woodward, with others, had laboured in the same field. In the Eighteenth Century, especially in its latter half, men's minds were busy about the physical agencies determining or modifying the features of the earth's crust; water and fire, subsidence from a primæval ocean and transformation by outbursts of the central heat, Neptune and Pluto, were being appealed to, by Werner on the one hand, and by Desmarest on the other, in explanation of the earth's phenomenon. The way was being prepared, theories and views were abundant, and many sound observations had been made; and yet the science of geology, properly so-called, the exact and proved knowledge of the successive phases of the world's life, may be said to date from the closing years of the Eighteenth Century.

In 1783, James Hutton put forward in a brief memoir his "Theory of the Earth," which in 1795, two years before his death, he expanded into a book; but his ideas failed to lay hold of men's minds until the century had passed away, when, in 1802, they found an able expositor in John Playfair. The very same year that Hutton published his theory, Cuvier came to Paris and almost forthwith began, with Brongniart, his immortal researches into the fossils of Paris and its neighbourhood. And four years later, in the year 1799 itself, William Smith's tabular list of strata and fossils saw the light. It is, I believe, not too much to say that out of these geology, as we now know it, has sprung. It was thus in the closing years of the Eighteenth Century that was began the work which the Nineteenth Century has carried forward to such great results. But at that time only the select few had grasped the truth, and even they only the beginning of it. Outside a narrow circle the thoughts, even of the educated, about the history of the globe, were bounded by the story of the Deluge—though the story was often told in a strange fashion—or were guided by the fantastic views of the plastic forces of a sportive Nature.

In another branch of science, in that which deals with the problems presented by living beings, the thoughts of men in 1779 were also very different from the thoughts of men to-day. It is a very old quest, the quest after the knowledge of the nature of living beings, one of the earliest on which man set out; for it promised to lead him to a knowledge of himself, a promise which perhaps is still before us, but the fulfilment of which is as yet far off. As time has gone on, the pursuit of natural knowledge has seemed to lead man away from himself into the furthermost parts of the universe, and into secret workings of Nature in which he appears to be of little or no account; and his knowledge of the nature of living things, and so of his own nature, has advanced slowly, waiting till the

progress of other branches of natural knowledge can bring it aid. Yet in the past hundred years, the biologic sciences, as we now call them, have marched rapidly onward.

We may look upon a living body as a machine doing work in accordance with certain laws, and may seek to trace out the working of the inner wheels, how these raise up the lifeless dust into living matter, and let the living matter fall away again into dust, giving out movement and heat. Or we may look upon the individual life as a link in a long chain, joining something which went before to something about to come, a chain whose beginning lies hid in the farthest past, and may seek to know the ties which bind one life to another. As we call up to view the long series of living forms, living now or flitting like shadows on the screen of the past, we may strive to lay hold of the influences which fashion the garment of life. Whether the problems of life are looked upon from the one point of view or the other, we to-day, not biologists only, but all of us, have gained a knowledge hidden even from the philosophers a hundred years ago.

Of the problems presented by the living body viewed as a machine, some may be spoken of as mechanical, others as physical, and yet others as chemical, while some are, apparently at least, none of these. In the Seventeenth Century, William Harvey, laying hold of the central mechanism of the blood stream, opened up a path of inquiry which his own age and the century which followed trod with marked success. The knowledge of the mechanics of the animal and of the plant advanced apace; but the physical and chemical problems had yet to wait. The Eighteenth Century, it is true, had its physics and its chemistry; but, in relation at least to the problems of the living being, a chemistry which knew not oxygen and a physics which knew not the electricity of chemical action were of little avail. The philosopher of 1799, when he discussed the functions of the animal or of the plant involving chemical changes, was fain for the most part, as were his predecessors in the century before, to have recourse to such vague terms as "fermentation" and the like; to-day our treatises on physiology are largely made up of precise and exact expositions of the play of physical agencies and chemical bodies in the living organism. He made use of the words "vital force" or "vital principle" not as an occasional, but as a common, explanation of the phenomena of the living body. During the present century, especially during its latter half, the idea embodied in those words has been driven away from one seat after another; if we use it now when we are dealing with the chemical and physical events of life we use it with reluctance, as a *deus ex machina* to be appealed to only when everything else has failed.

Some of the problems—and those, perhaps, the chief problems—of the living body have to be solved neither by physical nor by chemical methods, but by methods of their own. Such are the problems of the nervous system. In respect of these the men of 1799 were on the threshold of a pregnant discovery. During the latter part of the present century, and especially during its last quarter, the analysis of the mysterious processes in the nervous system, and especially in the brain, which issue as feeling, thought, and the power to move, has been pushed forward with a success conspicuous in its practical, and full of promise in its theoretical, gains. That analysis may be briefly described as a following up of threads. We now know that what takes place along a tiny thread which we call a nerve-fibre differs from that which takes place along its fellow threads, that differing nervous impulses travel along different nerve fibres, and that nervous and psychical events are the outcome of the clashing of nervous impulses as they sweep along the closely-woven web of living threads of which the brain is made. We have learnt by experiment and by observation that the pattern of the web determines the play of the impulses, and we can already explain many of the obscure problems not only of nervous disease, but of nervous life, by an analysis which

is a tracking out the devious and linked paths of nervous threads. The very beginning of this analysis was unknown in 1799. Men knew that nerves were the agents of feeling and of the movements of muscles; they had learnt much about what this part or that part of the brain could do; but they did not know that one nerve-fibre differed from another in the very essence of its work. It was just about the end of the past century, or the beginning of the present one, that an English surgeon began to ponder over a conception which, however, he did not make known until some years later, and which did not gain complete demonstration and full acceptance until still more years had passed away. It was in 1811, in a tiny pamphlet published privately, that Charles Bell put forward his "New Idea" that the nervous system was constructed on the principle that "the nerves are not single nerves possessing various powers, but bundles of different nerves, whose filaments are united for the convenience of distribution, but which are distinct in office as they are in origin from the brain."

Our present knowledge of the nervous system is to a large extent only an exemplification and expansion of Charles Bell's "New Idea," and has its origin in that.

If we pass from the problems of the living organism viewed as a machine to those presented by the varied features of the different creatures who have lived, or who still live on the earth, we at once call to mind that the middle years of the present century mark an epoch in biologic thought such as never came before, for it was then that Charles Darwin gave to the world the "Origin of Species."

That work, however, with all the far-reaching effects which it has had, could have had little or no effect, or, rather, could not have come into existence, had not the earlier half of the century been in travail preparing for its coming. For the germinal idea of Darwin appeals, as to witnesses, to the results of two lines of biologic investigation which were almost unknown to the men of the Eighteenth Century.

To one of these lines I have already referred. Darwin, as we know, appealed to the geological record; and we also know how that record, imperfect as it was then, and imperfect as it must always remain, has since his time yielded the most striking proofs of at least one part of his general conception. In 1799 there was, as we have seen, no geological record at all.

Of the other line I must say a few words.

To-day the merest beginner in biologic study, or even that exemplar of acquaintance without knowledge, the general reader, is aware that every living being, even man himself, begins its independent existence as a tiny ball, of which we can, even acknowledging to the full the limits of the optical analysis at our command, assert with confidence that in structure, using that word in its ordinary sense, it is in all cases absolutely simple. It is equally well known that the features of form which supply the characters of a grown-up living being, all the many and varied features of even the most complex organism, are reached as the goal of a road, at times a long road, of successive changes; that the life of every being, from the ovum to its full estate, is a series of shifting scenes, which come and go, sometimes changing abruptly, sometimes melting the one into the other, like dissolving views, all so ordained that often the final shape with which the creature seems to begin, or is said to begin, its life in the world is the outcome of many shapes, clothed with which it in turn has lived many lives before its seeming birth.

All or nearly all the exact knowledge of the laboured way in which each living creature puts on its proper shape and structure is the heritage of the present century. Although the way in which the chick is moulded in the egg was not wholly unknown even to the ancients, and in later years had been told, first in the Sixteenth Century by Fabricius, then in the Seventeenth Century in a more clear and striking manner by the great Italian naturalist Malpighi, the teaching thus offered had been neglected or

misinterpreted. At the close of the Eighteenth Century the dominant view was that in the making of a creature out of the egg there was no putting on of wholly new parts, no epigenesis. It was taught that the entire creature lay hidden in the egg, hidden by reason of the very transparency of its substance, lay ready-made but folded up, as it were, and that the process of development within the egg or within the womb was a mere unfolding, a simple evolution. Nor did men shrink from accepting the logical outcome of such a view—namely, that within the unborn creature itself lay in like manner, hidden and folded up, its offspring also, and within that again its offspring in turn, after the fashion of a cluster of ivory balls carved by Chinese hands, one within the other. This was no fantastic view put forward by an imaginative dreamer; it was seriously held by sober men, even by men like the illustrious Haller, in spite of their recognising that as the chick grew in the egg some changes of form took place. Though so early as the middle of the Eighteenth Century Friedrich Caspar Wolff and, later on, others had strenuously opposed such a view, it held its own not only to the close of the century, but far on into the next. It was not until a quarter of the present century had been added to the past that Von Baer made known the results of researches which once and for all swept away the old view. He and others working after him made it clear that each individual puts on its final form and structure not by an unfolding of pre-existing hidden features, but by the formation of new parts through the continued differentiation of a primitively simple material. It was also made clear that the successive changes which the embryo undergoes in its progress from the ovum to maturity are the expression of morphologic laws, that the progress is one from the general to the special, and that the shifting scenes of embryonic life are hints and tokens of lives lived by ancestors in times long past.

If we wish to measure how far off in biologic thought the end of the last century stands, not only from the end, but even from the middle of this one, we may imagine Darwin striving to write the "Origin of Species" in 1799. We may fancy him being told by philosophers explaining how one group of living beings differed from another group, because all its members and all their ancestors came into existence at one stroke when the first-born progenitor of the race, within which all the rest were folded up, stood forth as the result of a creative act. We may fancy him listening to a debate between the philosopher who maintained that all the fossils strewn in the earth were the remains of animals or plants churned up in the turmoil of a violent universal flood, and dropped in their places as the waters went away, and him who argued that such were not really the "spoils of living creatures," but the products of some playful plastic power, which out of the superabundance of its energy fashioned here and there the lifeless earth into forms which imitated, but only imitated, those of living things. Could he amid such surroundings by any flight of genius have beat his way to the conception for which his name will ever be known?

Here I may well turn away from the past. It is not my purpose, nor, as I have said, am I fitted, nor is this perhaps the place, to tell even in outline the tale of the work of science in the Nineteenth Century. I am content to have pointed out that the two great sciences of chemistry and geology took their birth, or at least began to stand alone, at the close of the last century, and have grown to be what we know them now within about a hundred years, and that the study of living beings has within the same time been so transformed as to be to-day something wholly different from what it was in 1799. And, indeed, to say more would be to repeat almost the same story about other things. If our present knowledge of electricity is essentially the child of the Nineteenth Century, so also is our present knowledge of many other branches of physics. And those most ancient forms of exact knowledge, the

knowledge of numbers and of the heavens, whose beginning is lost in the remote past, have, with all other kinds of natural knowledge, moved onward during the whole of the hundred years with a speed which is ever increasing. I have said, I trust, enough to justify the statement that in respect to natural knowledge a great gulf lies between 1799 and 1899. That gulf, moreover, is a two-fold one; not only has natural knowledge been increased, but men have run to and fro spreading it as they go. Not only have the few driven far back round the full circle of natural knowledge the dark clouds of the unknown which wrap us all about, but also the many walk in the zone of light thus increasingly gained. If it be true that the few to-day are, in respect to natural knowledge, far removed from the few of those days, it is also true that nearly all which the few alone knew then, and much which they did not know, has now become the common knowledge of the many.

What, however, I may venture to insist upon here is that the difference in respect to natural knowledge, whatever be the case with other differences between then and now, is undoubtedly a difference which means progress. The span between the science of that time and the science of to-day is beyond all question a great stride onwards.

We may say this, but we must say it without boasting. For the very story of the past which tells of the triumphs of science bids the man of science put away from him all thoughts of vainglory. And that by many tokens.

Whoever, working at any scientific problem, has occasion to study the inquiries into the same problem made by some fellow-worker in the years long gone by, comes away from that study humbled by one or other of two different thoughts. On the one hand he may find, when he has translated the language of the past into the phraseology of to-day, how near was his forerunner of old to the conception which he thought, with pride, was all his own, not only so true but so new. On the other hand, if the ideas of the investigator of old, viewed in the light of modern knowledge, are found to be so wide of the mark as to seem absurd, the smile which begins to play upon the lips of the modern is checked by the thought, Will the ideas which I am now putting forth, and which I think explain so clearly, so fully, the problem in hand, seem to some worker in the far future as wrong and as fantastic as do these of my forerunner to me? In either case his personal pride is checked. Further, there is written clearly on each page of the history of science, in characters which cannot be overlooked, the lesson that no scientific truth is born anew, coming by itself and of itself. Each new truth is always the offspring of something which has gone before, becoming in turn the parent of something coming after. In this aspect the man of science is unlike, or seems to be unlike, the poet and the artist. The poet is born, not made; he rises up, no man knowing his beginnings; when he goes away, though men after him may sing his songs for centuries, he himself goes away wholly, having taken with him his mantle, for this he can give to none other. The man of science is not thus creative; he is created. His work, however great it be, is not wholly his own; it is in part the outcome of the work of men who have gone before. Again and again a conception which has made a name great has come not so much by the man's own effort as out of the fulness of time. Again and again we may read in the words of some man of old the outlines of an idea which in later days has shone forth as a great acknowledged truth. From the mouth of the man of old the idea dropped barren, fruitless; the world was not ready for it, and heeded it not; the concomitant and abutting truths which could give it power to work were wanting. Coming back again in later days, the same idea found the world awaiting it; things were in travail preparing for it; and someone, seizing the right moment to put it forth again, leapt into fame. It is not so much the men of science who make science, as some spirit which, born of the truths already won, drives the man

of science onward, and uses him to win new truths in turn.

It is because each man of science is not his own master, but one of many obedient servants of an impulse which was at work long before him, and will work long after him, that in science there is no falling back. In respect to other things there may be times of darkness and times of light; there may be risings, decadences, and revivals. In science there is only progress. The path may not be always a straight line, there may be swerving to this side and to that, ideas may seem to return again and again to the same point of the intellectual compass; but it will always be found that they have reached a higher level—they have moved, not in a circle, but in a spiral. Moreover science is not fashioned as is a house, by putting brick to brick, that which is once put remaining as it was put to the end. The growth of science is that of a living being. As in the embryo phase follows phase, and each member of the body puts on in succession different appearances, though all the while the same member, so a scientific conception of one age seems to differ from that of a following age, though it is the same one in the process of being made; and as the dim outlines of the early embryo become, as the being grows more distinct and sharp, like a picture on a screen brought more and more into focus, so the dim gropings and searchings of the men of science of old are by repeated approximations wrought into the clear and exact conclusions of later times.

The story of natural knowledge, of science, in the nineteenth century, as, indeed, in preceding centuries, is, I repeat, a story of continued progress. There is in it not so much as a hint of falling back, not even of standing still. What is gained by scientific inquiry is gained for ever; it may be added to, it may seem to be covered up, but it can never be taken away. Confident that the progress will go on, we cannot help peering into the years to come and straining our eyes to foresee what science will become and what it will do as they roll on. While we do so, the thought must come to us, Will all the increasing knowledge of Nature avail only to change the ways of man—will it have no effect on man himself?

The material good which mankind has gained and is gaining through the advance of science is so imposing as to be obvious to everyone, and the praises of this aspect of science are to be found in the mouths of all. Beyond all doubt science has greatly lessened and has markedly narrowed hardship and suffering; beyond all doubt science has largely increased and has widely diffused ease and comfort. The appliances of science have, as it were, covered with a soft cushion the rough places of life, and that not for the rich only, but also for the poor. So abundant and so prominent are the material benefits of science that in the eyes of many these seem to be the only benefits which she brings. She is often spoken of as if she were useful and nothing more, as if her work were only to administer to the material wants of man.

Is this so?

We may begin to doubt it when we reflect that the triumphs of science which bring these material advantages are in their very nature intellectual triumphs. The increasing benefits brought by science are the results of man's increasing mastery over Nature, and that mastery is increasingly a mastery of mind; it is an increasing power to use the forces of what we call inanimate nature in place of the force of his own or other creatures' bodies; it is an increasing use of mind in place of muscle.

Is it to be thought that that which has brought the mind so greatly into play has had no effect on the mind itself? Is that part of the mind which works out scientific truths a mere slavish machine, producing results it knows not how, having no part in the good which in its working it brings forth;

What are the qualities, the features of that scientific

mind which has wrought, and is working, such great changes in man's relation to Nature? In seeking an answer to this question we have not to inquire into the attributes of genius. Though much of the progress of science seems to take on the form of a series of great steps, each made by some great man, the distinction in science between the great discoverer and the humble worker is one of degree only, not of kind. As I was urging just now, the greatness of many great names in science is often, in large part, the greatness of occasion, not of absolute power. The qualities which guide one man to a small truth silently taking its place among its fellows, as these go to make up progress, are at bottom the same as those by which another man is led to something of which the whole world rings.

The features of the fruitful scientific mind are in the main three.

In the first place, above all other things, his nature must be one which vibrates in unison with that of which he is in search; the seeker after truth must himself be truthful, truthful with the truthfulness of Nature. For the truthfulness of Nature is not wholly the same as that which man sometimes calls truthfulness. It is far more imperious, far more exacting. Man, unscientific man, is often content with "the nearly" and "the almost." Nature never is. It is not her way to call the same two things which differ, though the difference may be measured by less than the thousandth of a milligramme or of a millimetre, or by any other like standard of minuteness. And the man who, carrying the ways of the world into the domain of science, thinks that he may treat Nature's differences in any other way than she treats them herself, will find that she resents his conduct; if he in carelessness or in disdain overlooks the minute difference which she holds out to him as a signal to guide him in his search, the projecting tip, as it were, of some buried treasure, he is bound to go astray, and the more strenuous he struggles on, the farther will he find himself from his true goal.

In the second place, he must be alert of mind. Nature is ever making signs to us, she is ever whispering to us the beginnings of her secrets; the scientific man must be ever on the watch, ready at once to lay hold of Nature's hint however small, to listen to her whisper however low.

In the third place, scientific inquiry, though it be pre-eminently an intellectual effort, has need of the moral quality of courage—not so much the courage which helps a man to face a sudden difficulty as the courage of steadfast endurance. Almost every inquiry, certainly every prolonged inquiry, sooner or later goes wrong. The path, at first so straight and clear, grows crooked and gets blocked; the hope and enthusiasm, or even the jaunty ease, with which the inquirer set out, leave him, and he falls into a slough of despond. That is the critical moment calling for courage. Struggling through the slough he will find on the other side of the wicket-gate opening up the real path; losing heart he will turn back and add one more stone to the great cairn of the unaccomplished.

But, I hear some one say, these qualities are not the peculiar attributes of the man of science; they may be recognised as belonging to almost everyone who has commanded or deserved success, whatever may have been his walk of life. That is so. That is exactly what I would desire to insist, that the men of science have no peculiar virtues, no special powers. They are ordinary men, their characters are common, even commonplace. Science, as Huxley said, is organised common sense, and men of science are common men, drilled in the ways of common sense.

For their life has this feature. Though in themselves they are no stronger, no better than other men, they possess a strength which, as I have just now urged, is not their own, but is that of the science whose servants they are. Even in his apprenticeship the scientific inquirer,

while learning what has been done before his time, if he learns it aright, so learns it that what is known may serve him not only as a vantage ground whence to push off into the unknown, but also as a compass to guide him in his course. And when fitted for his work he enters on inquiry itself, what a zealous anxious guide, what a strict and—because strict—helpful school-mistress does Nature make herself to him! Under her care every inquiry, whether it bring the inquirer to a happy issue or seem to end in nought, trains him for the next effort. She so orders her ways that each act of obedience to her makes the next act easier for him, and step by step she leads him on towards that perfect obedience which is complete mastery.

Indeed, when we reflect on the potency of the discipline of scientific inquiry, we cease to wonder at the progress of scientific knowledge. The results actually gained seem to fall so far short of what under such guidance might have been expected to have been gathered in that we are fain to conclude that science has called to follow her, for the most part, the poor in intellect and the wayward in spirit. Had she called to her service the many acute minds who have wasted their strength struggling in vain to solve hopeless problems, or who have turned their energies to things other than the increase of knowledge; had she called to her service the many just men who have walked straight without the need of a rod to guide them, how much greater than it has been would have been the progress of science, and how many false teachings would the world have been spared! To men of science themselves, when they consider their favoured lot, the achievements of the past should serve not as a boast, but as a reproach.

If there be any truth in what I have been urging, that the pursuit of scientific inquiry is itself a training of special potency, giving strength to the feeble and keeping in the path those who are inclined to stray, it is obvious that the material gains of science, great as they may be, do not make up all the good which science brings or may bring to man. We especially, perhaps, in these later days, through the rapid development of the physical sciences, are too apt to dwell on the material gains alone. As a child in its infancy looks upon its mother only as a giver of good things, and does not learn till in after days how she was also showing her love by carefully training it in the way it should go, so we, too, have thought too much of the gifts of science, overlooking her power to guide.

Man does not live by bread alone, and science brings him more than bread. It is a great thing to make two blades of grass grow where before one alone grew; but it is no less great a thing to help a man to come to a just conclusion on the questions with which he has to deal. We may claim for science that while she is doing the one she may be so used as to do the other also. The dictum just quoted, that science is organised common sense, may be read as meaning that the common problems of life which common people have to solve are to be solved by the same methods by which the man of science solves his special problems. It follows that the training which does so much for him may be looked to as promising to do much for them. Such aid can come from science on two conditions only. In the first place, this her influence must be acknowledged; she must be duly recognised as a teacher no less than as a hewer of wood and a drawer of water. And the pursuit of science must be followed not by the professional few only, but, at least in such measure as will ensure the influence of example, by the many. But this latter point I need not urge before this great Association, whose chief object during more than half a century has been to bring within the fold of science all who would answer to the call. In the second place, it must be understood that the training to be looked for from science is the outcome not of the accumulation of scientific knowledge, but of the practice of scientific inquiry. Man may have at his fingers' ends all the accomplished results and all the current opinions of any one

or of all the branches of science, and yet remain wholly unscientific in mind; but no one can have carried out even the humblest research without the spirit of science in some measure resting upon him. And that spirit may in part be caught even without entering upon an actual investigation in search of a new truth. The learner may be led to old truths, even the oldest, in more ways than one. He may be brought abruptly to a truth in its finished form, coming straight to it like a thief climbing over the wall; and the hurry and press of modern life tempt many to adopt this quicker way. Or he may be more slowly guided along the path by which the truth was reached by him who first laid hold of it. It is by this latter way of learning the truth, and by this alone, that the learner may hope to catch something at least of the spirit of the scientific inquirer.

This is not the place, nor have I the wish, to plunge into the turmoil of controversy; but, if there be any truth in what I have been urging, then they are wrong who think that in the schooling of the young science can be used with profit only to train those for whom science will be the means of earning their bread. It may be that from the point of view of the pedagogic art the experience of generations has fashioned out of the older studies of literature an instrument of discipline of unusual power, and that the teaching of science is as yet but a rough tool in unpractised hands. That, however, is not an adequate reason why scope should not be given for science to show the value which we claim for it as an intellectual training fitted for all sorts and conditions of men. Nor need the studies of humanity and literature fear her presence in the schools, for if her friends maintain that that teaching is one-sided, and therefore misleading, which deals with the doings of man only, and is silent about the works of Nature, in the sight of which he and his doings shrink almost to nothing, she herself would be the first to admit that that teaching is equally wrong which deals only with the works of Nature and says nothing about the doings of man, who is, to us at least, Nature's centre.

There is yet another general aspect of science on which I would crave leave to say a word. In that broad field of human life which we call politics, in the struggle not of man with man, but of race with race, science works for good. If we look only on the surface it may at first sight seem otherwise. In no branch of science has there during these later years been greater activity and more rapid progress than in that which furnishes the means by which man brings death, suffering, and disaster on his fellow-men. If the healer can look with pride on the increased power which science has given him to alleviate human suffering and ward off the miseries of disease, the destroyer can look with still greater pride on the power which science has given him to sweep away lives and to work desolation and ruin; while the one has slowly been learning to save units, the other has quickly learnt to slay thousands. But, happily, the very greatness of the modern power of destruction is already becoming a bar to its use, and bids fair—may we hope before long?—wholly to put an end to it; in the words of Tacitus, though in another sense, the very preparations for war, through the character which science gives them, make for peace.

Moreover, not in one branch of science only, but in all, there is a deep undercurrent of influence sapping the very foundations of all war. As I have already urged, no feature of scientific inquiry is more marked than the dependence of each step forward on other steps which have been made before. The man of science cannot sit by himself in his own cave weaving out results by his own efforts, unaided by others, heedless of what others have done and are doing. He is but a bit of a great system, a joint in a great machine, and he can only work aright when he is in due touch with his fellow-workers. If his labour is to be what it ought to be, and is to have the weight which it ought to have, he must know what is being done, not by himself, but by others, and by others

not of his own land and speaking his tongue only, but also of other lands and of other speech. Hence it comes about that to the man of science the barriers of manners and of speech which pen men into nations become more and more unreal and indistinct. He recognises his fellow-worker, wherever he may live and whatever tongue he may speak, as one who is pushing forward shoulder to shoulder with him towards a common goal, as one whom he is helping and who is helping him. The touch of science makes the whole world kin.

The history of the past gives us many examples of this brotherhood of science. In the revival of learning throughout the Sixteenth and Seventeenth Centuries, and some way on into the Eighteenth Century, the common use of the Latin tongue made intercourse easy. In some respects in those earlier days science was more cosmopolitan than it afterwards became. In spite of the difficulties and hardships of travel, the men of science of different lands again and again met each other face to face, heard with their ears, and saw with their eyes what their brethren had to say or to show. The Englishman took the long journey to Italy to study there; the Italian, the Frenchman, and the German wandered from one seat of learning to another; and many a man held a chair in a country not his own. There was help, too, as well as intercourse. The Royal Society of London took upon itself the task of publishing nearly all the works of the great Italian Malpighi, and the brilliant Lavoisier, two years before his own countrymen in their blind fury slew him, received from the same body the highest token which it could give of its esteem.

In these closing years of the Nineteenth Century this great need of mutual knowledge and of common action felt by men of science of different lands is being manifested in a special way. Though now-a-days what is done anywhere is soon known everywhere, the news of a discovery being often flashed over the globe by telegraph, there is an increasing activity in the direction of organisation to promote international meetings and international co-operation. In almost every science inquirers from many lands now gather together at stated intervals in international congresses to discuss matters which they have in common at heart and go away, each one feeling strengthened by having met his brother. The desire that in the struggle to lay bare the secrets of Nature the least waste of human energy should be incurred is leading more and more to the concerted action of nations combining to attack problems, the solution of which is difficult and costly. The determination of standards of measurement, magnetic surveys, the solution of great geodetic problems, the mapping of the heavens and of the earth—all these are being carried on by international organisations.

In this and in other countries men's minds have this long while past been greatly moved by the desire to make fresh efforts to pierce the dark secrets of the forbidding Antarctic regions. Belgium has just made a brave single-handed attempt; a private enterprise sailing from these shores is struggling there now, lost for the present to our view; and this year we in England and our brethren in Germany are, thanks to the promised aid of the respective Governments, and no less to private liberality, in which this Association takes its share, able to begin the preparation of carefully organised expeditions. That international amity of which I am speaking is illustrated by the fact that in this country, and in that there is not only a great desire, but a firm purpose, to secure the fullest co-operation between the expeditions which will leave the two shores. If in this momentous attempt any rivalry be shown between the two nations, it will be for each a rivalry, not in forestalling, but in assisting the other. May I add that if the story of the past may seem to give our nation some claim to the seas as more peculiarly our own, that claim bespeaks a duty likewise peculiarly our own to leave no effort untried by which we may plumb the seas' yet unknown depths, and trace their yet unknown shores? That claim, if it means anything, means that when nations are

joining hands in the dangerous work of exploring the unknown South, the larger burden of the task should fall to Britain's share; it means that we in this country should see to it, and see to it at once, that the concerted Antarctic expedition which in some two years or so will leave the shores of Germany, of England, and, perhaps, of other lands, should, so far as we are concerned, be so equipped and so sustained that the risk of failure and disaster may be made as small, and the hope of being able not merely to snatch a hurried glimpse of lands not yet seen, but to gather in with full hands a rich harvest of the facts which men not of one science only, but of many, long to know, as great as possible.

Another international scientific effort demands a word of notice. The need which every inquirer in science feels to know, and to know quickly, what his fellow-worker, wherever on the globe he may be carrying on his work or making known his results, has done or is doing, led some four years back to a proposal for carrying out by international co-operation a complete current index, issued promptly, of the scientific literature of the world. Though much labour in many lands has been spent upon the undertaking, the project is not yet an accomplished fact. Nor can this, perhaps, be wondered at, when the difficulties of the task are weighed. Difficulties of language, difficulties of driving in one team all the several sciences which, like young horses, wish each to have its head free with leave to go its own way, difficulties mechanical and financial of press and post, difficulties raised by existing interests—these and yet other difficulties are obstacles not easy to be overcome. The most striking and the most encouraging features of the deliberations which have now been going on for three years have been the repeated expressions, coming not from this or that quarter only, but from almost all quarters, of an earnest desire that the effort should succeed, of a sincere belief in the good of international co-operation, and of a willingness to sink as far as possible individual interests for the sake of the common cause. In the face of such a spirit we may surely hope that the many difficulties will ultimately pass out of sight.

Perhaps, however, not the least notable fact of international co-operation in science is the proposal which has been made within the last two years that the leading academies of the world should, by representatives, meet at intervals to discuss questions in which the learned of all lands are interested. A month hence a preliminary meeting of this kind will be held at Wiesbaden; and it is at least probable that the closing year of that Nineteenth Century in which science has played so great a part may, at Paris during the great World's Fair—which every friend, not of science only, but of humanity, trusts may not be put aside or even injured through any untoward event, and which promises to be an occasion not of pleasurable sight-seeing only, but also, by its many international congresses, of international communing in the search for truth—witness the first select Witenagemote of the science of the world.

I make no apology for having thus touched on international co-operation. I should have been wanting, had I not done so, to the memorable occasion of this meeting. A hundred years ago two great nations were grappling with each other in a fierce struggle, which had lasted, with pauses, for many years, and was to last for many years to come; war was on every lip and in almost every heart. To-day this meeting has, by a common wish, been so arranged that those two nations should, in the persons of their men of science, draw as near together as they can, with nothing but the narrow streak of the Channel between them, in order that they may take counsel together on matters in which they have one interest and a common hope. May we not look upon this brotherly meeting as one of many signs that science, though she works in a silent manner and in ways unseen by many, is steadily making for peace?

Looking back, then, in this last year of the eighteen hundreds, on the century which is drawing to its close, while we may see in the history of scientific inquiry much which, telling the man of science of his short-comings and his weakness, bids him be humble, we also see much, perhaps more, which gives him hope. Hope is indeed one of the watchwords of science. In the latter-day writings of some who know not science, much may be read which shows that the writer is losing or has lost hope in the future of mankind. There are not a few of these; their repeated utterances make a sign of the times. Seeing in matters lying outside science few marks of progress and many tokens of decline or of decay, recognising in science its material benefits only, such men have thoughts of despair when they look forward to the times to come. But if there be any truth in what I have attempted to urge to-night, if the intellectual, if the moral influences of science are no less marked than her material benefits, if, moreover, that which she has done is but the earnest of that which she shall do, such men may pluck up courage and gather strength by laying hold of her garment. We men of science at least need not share their views or their fears. Our feet are set, not on the shifting sands of the opinions and of the fancies of the day, but on a solid foundation of verified truth, which by the labours of each succeeding age is made broader and more firm. To us the past is a thing to look back upon, not with regret, not as something which has been lost never to be regained, but with content, as something whose influence is with us still, helping us on our further way. With us, indeed, the past points not to itself, but to the future; the golden age is in front of us, not behind us; that which we do know is a lamp whose brightest beams are shed into the unknown before us, showing us how much there is in front and lighting up the way to reach it. We are confident in the advance because, as each one of us feels that any step forward which he may make is not ordered by himself alone, and is not the result of his own sole efforts in the present, but is, and that in large measure, the outcome of the labours of others in the past, so each one of us has the sure and certain hope that as the past has helped him, so his efforts, be they great or be they small, will be a help to those to come.

SOLID HYDROGEN.*

By JAMES DEWAR, F.R.S., &c.

IN the autumn of 1898, after the production of liquid hydrogen was possible on a scale of one or two hundred c.c., its solidification was attempted under reduced pressure. At this time, to make the isolation of the hydrogen as effective as possible, the hydrogen was placed in a small vacuum test-tube, placed in a larger vessel of the same kind. Excess of the hydrogen partly filled the circular space between the two vacuum vessels. The apparatus is shown in Fig. 1. In this way the evaporation was mainly thrown on the liquid hydrogen in the annular space between the tubes. In this arrangement the outside surface of the smaller tube was kept at the same temperature as the inside, so that the liquid hydrogen for the time was effectually guarded from influx of heat. With such a combination the liquid hydrogen was evaporated under some 10 m.m. pressure, yet no solidification took place. Seeing experiments of this kind required a large supply of the liquid; other problems were attacked, and any attempts in the direction of producing the solid for the time abandoned. During the course of the present year many varieties of electric resistance thermometers have been under observation, and with some of these the reduction of temperature brought about by exhaustion was investigated. Thermometers constructed

* Read before the British Association (Section B), Dover Meeting, 1899.

of platinum and platinum-rhodium (alloy) were only lowered $1\frac{1}{2}^{\circ}$ C. by exhaustion of the liquid hydrogen, and they all gave a boiling-point of -245° C., whereas the reduction in temperature by evaporation *in vacuo* ought to be 5° C., and the true boiling-point from -252° to -253° C. In the course of these experiments it was noted that almost invariably there was a slight leak of air, which became apparent by its being frozen into an air snow in the interior of the vessel, where it met the cold vapour of hydrogen coming off. When conducting wires covered with silk have to pass through india-rubber corks it is very difficult at these excessively low temperatures to prevent leaks, when corks get as hard as a stone, and cements crack in all directions. The effect of this slight air leak on the liquid hydrogen when the pressure got reduced below 60 m.m. was very remarkable, as it suddenly solidified into a white froth-like mass like frozen foam. My first impressions were that this body was a sponge of solid air containing the liquid hydrogen, just like ordinary air, which is a magma of solid nitrogen containing liquid oxygen. The fact, however, that this white solid froth evaporated completely at the low pressure without leaving any substantial amount of solid air led to the conclusion that the body after all must be solid hydrogen. This surmise was confirmed by observing that if the pressure, and therefore the temperature, of the hydrogen was allowed to rise, the solid melted when the pressure reached about 55 m.m.

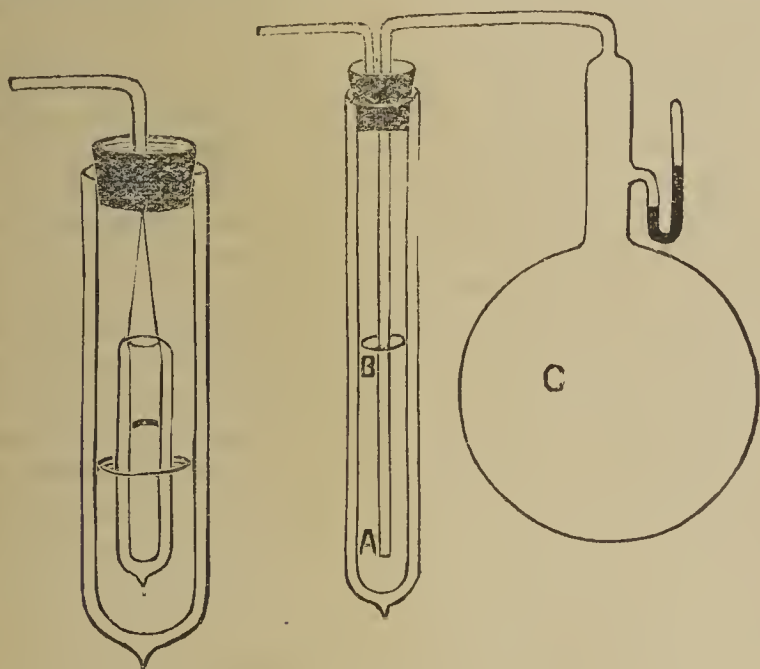


Fig 1.

Fig 2.

The failure of the early experiment must then have been due to supercooling of the liquid, which is prevented in this case by contact with metallic wires and traces of solid air. To settle the matter definitely the following experiment was arranged. A flask C of about a litre capacity, to which a long glass tube bent twice at right angles was sealed, as shown in Fig. 2, and to which a small mercury manometer can be sealed, was filled with pure dry hydrogen and sealed off. The lower portion AB of this tube was calibrated. It was surrounded with liquid hydrogen placed in a vacuum vessel arranged for exhaustion. As soon as the pressure got well reduced below that of the atmosphere, perfectly clear liquid hydrogen began to collect in the tube AB, and could be observed accumulating until, about 30 to 40 m.m. pressure, the liquid hydrogen surrounding the outside of the tube suddenly passed into a solid white foam-like mass, almost filling the whole space. As it was not possible to see the condition of the hydrogen in the interior of the tube AB when it was covered with a large quantity of this solid, the whole apparatus was turned upside down in order to see whether any liquid would run down AB into the flask C. Liquid did not flow down the tube, so the liquid hydrogen with which the tube was partly filled must have solidified. By placing a strong light on the side of the vacuum test-tube opposite the eye, and maintaining the

exhaustion to about 25 m.m., gradually the solid became less opaque, and the material in AB was seen to be a transparent ice in the lower part, but the surface looked frothy. This fact prevented the solid density from being determined, but the maximum fluid density has been approximately ascertained. This was found to be 0.086, the liquid at its boiling-point having the density 0.07. The solid hydrogen melts when the pressure of the saturated vapour reaches about 55 m.m. In order to determine the temperature two constant volume hydrogen thermometers were used. One at 0° C. contained hydrogen under a pressure of 269.8 m.m., and the other under a pressure of 127 m.m. The mean temperature of the solid was found to be 16° absolute under a pressure of 35 m.m. All the attempts made to get an accurate electric resistance thermometer for such low temperature observations have been so far unsatisfactory. Now that pure helium is definitely proved to be more volatile than hydrogen, this body, after passing through a spiral glass tube immersed in liquid hydrogen to separate all other gases, must be compared with the hydrogen thermometer. For the present the boiling-point which is 21° absolute at 760 m.m., compared with the boiling-point at 35 m.m. or 16° absolute, enables the following approximate formula for the vapour tension of liquid hydrogen below one atmosphere pressure to be derived:—

$$\log p = 6.7341 - 83.28/T \text{ m.m.,}$$

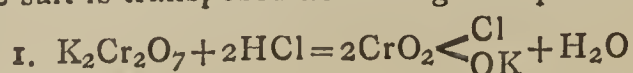
where T = absolute temperature, and the pressure is in m.m. This formula gives us for 55 m.m. a temperature of 16.7° absolute. The melting-point of hydrogen must therefore be about 16° or 17° absolute. It has to be noted that the pressure in the constant volume hydrogen thermometer, used to determine the temperature of solid hydrogen boiling under 35 m.m., had been so far reduced that the measurements were made under from one-half to one-fourth the saturation pressure for the temperature. When the same thermometers were used to determine the boiling-point of hydrogen at atmospheric pressure, the internal gas pressure was only reduced to one-thirteenth the saturation pressure for the temperatures. The absolute accuracy of the boiling-points under diminished pressure must be examined in some future paper. The practical limit of temperature we can command by the evaporation of solid hydrogen is from 14° to 15° absolute. In passing it may be noted that the critical temperature of hydrogen being 30° to 32° absolute, the melting-point is about half the critical temperature. The melting-point of nitrogen is also about half its critical temperature. The foam-like appearance of the solid when produced in an ordinary vacuum is due to the small density of the liquid, and the fact that rapid ebullition is substantially taking place in the whole mass of liquid. The last doubt as to the possibility of solid hydrogen having a metallic character has been removed, and for the future hydrogen must be classed among the non-metallic elements.

Estimation of Mannose mixed with other Sugars.—Em. Bourquelot and H. Hérissé.—During researches on the composition of certain albumens, the authors were led to investigate in what measure the property possessed by mannose of giving a hydrazone insoluble in the cold could be used for an estimation of this sugar. To do this, a series of experiments were made on solutions containing known quantities of mannose mixed with other sugars. The quantity of mannose hydrazine precipitated was determined and compared with the original quantity of mannose. It was found that phenylhydrazine can be used to estimate mannose in researches in vegetable chemistry, and that the presence of other sugars does not sensibly modify the results. As low a temperature as possible should be used, and only solutions containing from 3 to 6 per cent of mannose.—*Comptes Rendus*, cxxix., No. 6.

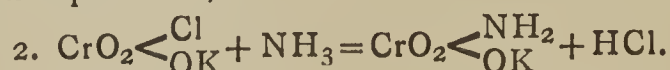
ON CHROMYLAMIDE, $\text{CrO}_2\text{<}\begin{smallmatrix} \text{NH}_2 \\ \text{NH}_2 \end{smallmatrix}$.

By JULIUS OHLY, Ph.D.

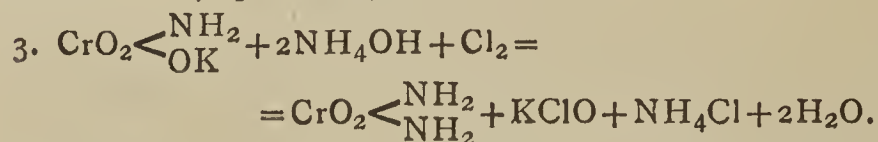
If bichromate of potassium is warmed with hydrochloric acid, the salt is transposed according to Equation 1:—



into potassium chlorochromate and water. Heintze succeeded in producing a substitution-product of the formula $\text{CrO}_2\text{<}\begin{smallmatrix} \text{NH}_2 \\ \text{OK} \end{smallmatrix}$, and of dark ruby colour, by treating the chlorochromate obtained in 1 with dry ammonia gas, as shown in Equation 2,—



He has described his method of preparing the salt, and by following his directions closely I also obtained it. If the product resulting under these conditions is dissolved in distilled water, a concentrated solution of ammonia (aqueous) added, and the mixture covered with a layer of ether, and dry chlorine gas conducted into it at common temperature, a lively reaction sets in, in the course of which the solution assumes a light brown colour and becomes clear (Equation 3):—



On letting this solution stand for forty-eight hours, yellowish brown, dull, metallic leaflets crystallised out.

They proved to be the expected chromylamide, which was found to be soluble in water, and to produce ammonia in plenty when rubbed together with soda-lime in a mortar. The solution of the amide in water was tested with silver nitrate and lead acetate, and gave the characteristic reactions of the amides.

Repeated analyses, the one made by decomposing a weighed quantity of the amide by means of hydrochloric acid and subsequent precipitation, the other by decomposing the compound through heat, which is very readily accomplished, showed it to be chromylamide, corresponding to the formula $\text{CrO}_2\text{<}\begin{smallmatrix} \text{NH}_2 \\ \text{NH}_2 \end{smallmatrix}$.

I have also tried to obtain the corresponding manganese compound, so far, however, with but indifferent success.

ACTION OF NITRATE OF SILVER ON THE FATTY ACIDS OF COTTON-SEED OIL.

By EUG. CHARABOT and M. MARCH.

M. MILLIAU has proposed a method for the detection of cotton-seed oil in olive oil, which is a great improvement on that of M. Becchi. This latter consisted, as will be remembered, of roughly treating the suspected oil with nitrate of silver. M. Milliau submits, not the oil itself, but its products of saponification to the action of the same reagent. Neither of the above-mentioned chemists, however, have attempted to establish the nature of the brown precipitate obtained by this treatment.

In 1895, M. Dupont (*Bull. Soc. Chim.*, Series 3, vol. xiii., pp. 696 and 775), in the course of a research on cotton-seed oil and its detection in American lards, discovered in this oil a volatile sulphurised substance.

Shortly afterwards, M. Dupont and one of us (Dupont and Charabot, *Bull. Soc. Chim.*, series 3, vol. xv., p. 341) met with an analogous volatile sulphide in authentic olive oil. They concluded that the black precipitate obtained with nitrate of silver might contain sulphide of silver, and that consequently the formation of a similar precipitate would not be an invariable proof of fraud. No experiment, however, was made with a view to determining its

chemical composition. We have therefore undertaken to decide this question.

Before commencing the study of the brown substance, which occurs when the fatty acids of cotton-seed oil are treated with nitrate of silver, it was interesting to find out whether, in the course of the preparation of these fatty acids, the sulphurised substance discovered by M. Dupont would be eliminated or not.

For preparing the fatty acids we followed the method described by MM. Müntz, Durand, and Milliau, in their masterly report to the Minister of Agriculture (*Bull. du Ministère de l'Agriculture*, 1895, p. 143). The product obtained was washed a great number of times with distilled water until the complete elimination of the sulphuric acid.

About 5 grms. of the thus purified fatty acid were oxidised by heating for six hours with a pure concentrated solution of permanganate of potash on a water-bath; the oxide of manganese was then dissolved in pure warm hydrochloric acid; the fatty acids were separated by filtration, and the clear liquid concentrated by evaporation.

The addition of nitrate of barium caused the formation of a precipitate of sulphate of barium insoluble in acids; thus the sulphurised matter in the cotton-seed oil was not eliminated during the preparation of the fatty acids.

We repeated the operation without using sulphuric acid, but using hydrochloric acid, which had already been tested and found perfectly pure. The results obtained were just as conclusive.

About 50 grms. of cotton-seed oil were then saponified, the fatty acids set at liberty, purified and treated with 3 per cent nitrate of silver on the water-bath; this placed us under exactly the conditions described by M. Milliau. A brown precipitate is formed, which we allowed to cool away from the light; this was collected on a filter, and washed a number of times with warm water.

The fatty acids were removed from the precipitate remaining on the filter by washing with alcohol at 90°; the insoluble product was then exhausted successively with ligroin, benzene free from thiophene, and ether. There finally remained a dark brown, homogeneous dry substance. This substance was powdered, and then treated with warm, dilute hydrochloric acid; very gradually a precipitate of chloride of silver was formed, and at the same time a fatty acid set at liberty.

This fatty acid, after being purified by solution in benzene and filtration of the solution, melts at 52° and solidifies at 49–50°. It gives a white ammoniacal salt, which, treated with nitrate of silver, gives a brown precipitate analogous to that from which it started.

Another portion of the brown precipitate, obtained by the action of nitrate of silver on the fatty acids of cotton-seed oil, was oxidised by heating for two hours with a pure concentrated solution of permanganate of potash on the water-bath. The oxide of manganese was dissolved by the addition of hydrochloric acid. Small oily drops collect on the surface of the liquid, and a precipitate of chloride of silver is formed; the solution is filtered and concentrated by evaporation. On adding nitrate of barium a precipitate of sulphate of barium is formed; this precipitate is very apparent, even when operating on only 1 grm. of the brown substance.

To sum up—1. The fatty acids obtained by the saponification of cotton-seed oil and precipitation by means of mineral acids are not free from sulphurised material. 2. The brown precipitate formed, when we treat these acids with nitrate of silver, contains principally the silver salt of an acid fusible at 52° and sulphide of silver.

Olive oil, which contains a sulphurised substance analogous to that of cotton-seed oil, would therefore be susceptible of giving with nitrate of silver a more or less distinct black precipitate of sulphide of silver. It is, therefore, unnecessary to insist too much on the care with which opinions should be formed when we have to deal with the search for cotton-seed oil in olive oil.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 11.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JULY 31ST, 1899.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, August 10th, 1899.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 208 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from July 1st to July 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 208 samples examined by us during the month, all were found to be clear, bright, and well filtered.

We have to record a continuation of the drought. Rain has fallen at Oxford on nine days only, the total amount being 1.32 inches, of which 0.76 inch, or more than half, fell on the 22nd. As the average amount for thirty years is 2.68 inches, we have a deficiency of 1.36 inches. This makes a total deficiency for the year of 3.11 inches, or 22.7 per cent.

Our bacteriological examinations of 383 samples have given the results recorded in the following table; we have also examined 39 other samples, from special wells, standpipes, &c., making a total of 422 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	1858
New River, filtered (mean of 77 samples) ..	30
Thames, unfiltered (mean of 26 samples) ..	1270
Thames water, from the clear water wells of eight Thames-derived supplies (mean of 203 samples)	41
Ditto ditto highest	430
Ditto ditto lowest	1
River Lea, unfiltered (mean of 26 samples) ..	4357
River Lea, from the East London Company's clear water well (mean of 25 samples) . . .	26

It has always seemed to us to be both unfair and misleading to test the bacterial quality of a water from an examination of a sample drawn from a standpipe or fire plug. The only correct, and by far the most direct test of efficient microbic purification by any filtration process, is to secure samples of the water immediately after filtration and before it passes into the distributing mains.

However good water may be at its source, it will always deteriorate more or less in the mains. This will occur with any supply, whether it be derived from the Thames, from Wales, or from chalk wells. There is no known mode of avoiding bacterial increase after the water passes into the mains and pipes of a great city like London; that is to say, the number of microbes always largely increases during its wide distribution and circulation through the labyrinth of pipes; but the additional microbes so generated are known by experience and observation to be harmless.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 7, August 14, 1899.

Researches on Metallic Derivatives of Acetylene.—MM. Berthelot and Delépine.—The authors have experimented on the compounds of acetylene with silver, silver nitrate, sulphate, chloride, and iodide. When heated in a vacuum, dry silver acetylide, Ag_2C_2 , detonates, with formation of a reddish flame. This flame is scarcely to be expected, since the products of the explosion are solids, silver and carbon. However, investigation of this matter leads to the conclusion that the temperature of the reaction is high enough to volatilise the carbon, and that the flame is gaseous carbon at a very high temperature, probably approaching 4000°C .

Reaction of Argon and Nitrogen with Mercury Alkyls.—M. Berthelot.—When mercury methyl, $\text{Hg}(\text{CH}_3)_2$, is placed in an atmosphere of argon and subjected to the silent electric discharge no compound with argon is formed, but when the argon is replaced by nitrogen a rapid absorption of the latter takes place.

Action of Sodammonium and Potassammonium on Tellurium and Sulphur.—C. Hugot.—In the presence of excess of the alkali two amorphous tellurides are formed, Na_2Te and K_2Te , both being white and insoluble in liquid ammonia gas. By making use of this latter property, the tellurides are separated from excess of ammonium alkali. By merely substituting sulphur for tellurium, the two monosulphides Na_2S and K_2S are formed. When tellurium is used in large excess, the tellurides Na_2Te_3 and K_2Te_3 are formed, which resemble the former in appearance. In the case of excess of sulphur being used, Na_2S_5 and Na_2Te_3 are formed, which absorb ammonia gas.

Estimation of Free Phosphorus in Oils and Fatty Bodies.—E. Louise.—The author proposes the following method for the estimation of free phosphorus in fatty substances, since it is available even when the phosphorus exists in mere traces:—A concentrated solution of silver nitrate is added to the oil in the presence of about twenty times its volume of acetone. The black precipitate obtained is, all other things being equal, proportional to the quantity of free phosphorus present in the oil. Acetone possesses the property of dissolving both oil and water at the same time, hence the drops of aqueous solution necessary to precipitate the phosphorus do not separate out.

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DAVID LEWIS, Treasurer.

Treasurer's Chambers, 20, York Place,
Edinburgh, August 1, 1899.

THE CHEMICAL NEWS.

VOL. LXXX., No. 2078.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

DOVER, 1899.

By HORACE T. BROWN, LL.D., F.R.S.
President of the Section.

THE subject which I have chosen for my Address is the fixation of carbon by plants, one which is the common meeting ground of Chemistry, Physics, and Biology. I must, however, confine myself only to certain aspects of the question, since it is manifestly impossible to fully discuss the whole of a subject of such magnitude and importance within the time at my disposal.

We have become so accustomed to the idea that the higher plants derive *the whole* of their carbon from atmospheric sources, that we are apt to forget how very indirect is the nature of much of the experimental evidence on which this belief is founded. There can, of course, be no doubt that the primary source of the organic carbon of the soil, and of the plants growing on it, is the atmosphere; but of late years there has been such an accumulation of evidence tending to show that the higher plants are capable of being nourished by the direct application of a great variety of ready-formed organic compounds, that we are justified in demanding further proof that the stores of organic substances in the soil must necessarily be oxidised down to the lowest possible point before their carbon is once more in a fit state to be assimilated.

It was the hope of gaining more direct evidence on this important question which led me some time ago to attack the problem experimentally in conjunction with Mr. F. Escombe, the resources of the Jodrell Laboratory at Kew having been kindly put at our disposal by Sir W. Thiselton Dyer and Dr. D. H. Scott. Up to the present time our experiments have not been carried far enough to enable us to give a positive answer to the main question, but they have already suggested a new method of attack which will enable us in the future to determine, with a fair amount of certainty, whether any particular plant, growing under perfectly natural conditions, derives any appreciable portion of its carbon from any other source than the gaseous carbon dioxide of the atmosphere.

During the course of the inquiry many interesting side issues have been raised which we believe to be of some importance in their bearing on the processes of plant nutrition, and it is to a consideration of these that I intend to devote the greater part of my Address.

I must, however, in the first place indulge in a little historical retrospect, and am the more tempted to do this, as far as the early pioneers in this branch of knowledge are concerned, since a critical study of their writings has shown me very clearly that the relative merits of some of these older workers, and the respective parts which they took in founding the true theory of assimilation, have in our own time been much misrepresented by more than one historian of science whose name carries great weight.

There is no chapter in the history of scientific discovery of greater abiding interest than that which was opened by Priestley in 1771, when he commenced his work on the influence of plants on the composition of the air around them. It has often been assumed that these experiments of Priestley, which were unquestionably the starting-point for all succeeding workers, were the result of some haphazard method of working, and of one of those happy chances to which he is in the habit of attri-

bute some of his most important discoveries. However much the element of chance entered into some of his work—and in this respect I think Priestley often does himself injustice—the discovery of the amelioration of vitiated air by plants was certainly not a case of this kind. Of all his contemporaries belonging to the old school of Chemistry Priestley had the clearest conception of the processes of animal respiration and of their identity with the process of combustion. This is clearly shown by his "Observations on Respiration and the Use of the Blood," which he presented to the Royal Society in 1776. This memoir, written of course from the phlogistic point of view, only requires translating into the language of the newer Chemistry to be an accurate statement of the main facts of animal respiration. We have it on Priestley's own authority that it was these studies which produced in his mind a conviction that there must be some provision in Nature for dephlogisticating the air which was constantly being vitiated by the processes of respiration, combustion, and putrefaction, and for rendering it once more fit for maintaining animal life. In his search for this compensating influence, which he justly regarded as one of the most important problems of natural philosophy, he made many attempts to bring back the vitiated air to its original state by agitating it with water, and by submitting it to the continued action of light and heat, and it was in the course of these systematic attempts that he was led to study the influence of plants in this direction.

It was in the month of August, 1771, that he made the memorable experiments at Leeds of immersing sprigs of mint in air which had been vitiated by the burning of a candle or by animal respiration. To quote his own words, this observation led him "to conclude that plants, instead of affecting the air in the same manner with animal respiration, reverse the effects of breathing, and tend to keep the atmosphere sweet and wholesome when it is become noxious in consequence of animals either living or breathing, or dying and putrefying in it." That he was fully convinced that these observations, which he repeated and amplified in the following year, presented the true key to the problem, is sufficiently shown by another passage in which he says:—"These proofs of the partial restoration of air by plants in a state of vegetation, though in a confined and unnatural situation, cannot but render it highly probable that the injury which is continually done to the atmosphere by the respiration of such a number of animals, and the putrefaction of such masses of both vegetable and animal matter, is, in part at least, repaired by the vegetable creation; and notwithstanding the prodigious mass of air that is corrupted daily by the above causes, yet if we consider the immense profusion of vegetables upon the face of the earth growing in places suited to their nature, and consequently at full liberty to exert all their powers, both inhaling and exhaling, it can hardly be thought but that it may be a sufficient counterbalance to it, and that the remedy is adequate to the evil."

Between the time of Priestley temporarily relinquishing his experiments in this direction in 1772, and his resumption of them in 1778, owing to the adverse criticism of Scheele and others, he had discovered dephlogisticated air or oxygen, and had elaborated his method for ascertaining the purity of air, or its richness in oxygen, by determining its diminution in volume after mixing with an excess of nitric oxide over water.* This method gave of course a much greater degree of precision to his results than was attainable in his earlier work, where the purity of the air at the end of an experiment was only determined by ascertaining if it would support the combustion of a candle or allow a small animal to live in it.

The results of his later work were published in 1799, and were not altogether confirmatory of those arrived at six years before. It is true that he generally found

* Nitric oxide was discovered by Priestley in 1772, and was described by him under the name of "nitrous air."

evidence of an evolution of oxygen by the plants, but occasionally the air was less "pure" at the end of an experiment than it was at the beginning, and this occurred in a sufficient number of cases to lead Priestley to doubt to some extent the accuracy of his previous conclusions. On the whole, however, he still thinks it *probable* that the vegetation of healthy plants has a salutary effect on the air in which they grow.

The reason for this want of complete consistency in these later experiments was, of course, his failure at that time to recognise the important influence of *light* in bringing about the evolution of oxygen, an explanation which was given shortly afterwards by Ingen-Housz.

Priestley's attention was now taken up with another observation, which led him within a very short distance indeed of the discovery that the evolution of oxygen by plants is conditioned not only by a sufficient degree of illumination, but also by the pre-existence of carbon dioxide. It is the more necessary to treat of this point somewhat in detail, since it is a part of his work which has received but scanty justice at the hands of recent writers, who have apparently failed to see how much our modern conceptions of plant nutrition really owe to the initiative of Priestley. In his "History of Botany," Sachs deals very unfairly with Priestley in this respect, owing to a want of intimate knowledge of his writings, and to the lack of anything like perspective in estimating the relative merits of his contemporaries Ingen-Housz and Senebier, whose position can only be completely understood after a careful study of their numerous original memoirs, some of which are by no means readily accessible.

In the course of his experiments on plants partially immersed in water more or less fully impregnated with "fixed air," Priestley had observed a fact which had not escaped the notice of Bonnet at an earlier date, that bubbles of gas arose spontaneously from the leaves and stems, and it occurred to him that an examination of the nature of this gas by means of his new eudiometric process ought to settle the question whether plants really do contribute in any way to the purification of ordinary air. It was in June, 1778, that he put this to the test, and he found that the air thus liberated was much richer in oxygen than ordinary air. On removing the plants he found to his astonishment that the water in which they had been placed, and which had a considerable amount of "green matter" adhering to the sides of the phials, still continued to evolve a gas which increased in amount when the vessels were placed in sunlight. On testing this gas with his eudiometric process, he found that it consisted to a great extent of "dephlogisticated air" or oxygen; in fact, from the experimental results which he gives, it is evident that the gas contained from 74 to 85 per cent of oxygen. Having observed that the "green matter" appeared much more readily in pump water than in rain or river water, and knowing that pump water contained considerable amounts of "fixed air," he was led to make a series of experiments with water artificially impregnated with carbon dioxide, which left no doubt in his mind that the production of the "green matter" and the evolution of dephlogisticated air were in some way due to the presence of "fixed air." Up to this point Priestley was following a path which seemed about to lead him to a complete solution of his previous difficulties. He had beyond all question succeeded in showing that the evolution of oxygen was not only dependent on the pre-existence of carbon dioxide, but that light was also required for the process. It only wanted, in fact, the recognition of the vegetable nature of the alga which constituted his "green substance" to bring these observations into line with his previous work, and to complete a discovery which would have eclipsed in importance all the others with which Priestley's name is associated. It was just this one step which he most provokingly failed to take. It is true that he examined the "green substance" under the microscope, but owing to want of skill in the use of the instru-

ment, and also to his defective eyesight, he was unable to determine its true nature, and unfortunately adopted the view that it had merely a mechanical action in separating the oxygen from the water, and, to use his own words, that "it was only a circumstance preceding the spontaneous emission of the air from water." He was in fact now inclined to regard the process as a purely chemical one, due to the direct action of light on the carbon dioxide dissolved in the water.

But this was by no means Priestley's final view, as shown by a further description of his experiments on plants set forth in the new edition of his works published in 1790, where he clearly recognised the error into which he had been led.* Meanwhile the subject had been taken up by two other observers, Ingen-Housz and Senebier, and in order to thoroughly understand the respective shares which these men took in advancing our knowledge of the assimilatory process, it is necessary to consult not only their books, but also the numerous scattered memoirs which appeared at intervals between the years 1779 and 1800.

To Ingen-Housz must unquestionably be awarded the merit of having experimentally demonstrated that the amelioration of the surrounding air by plants is not—as Priestley at first believed—due to vegetative action *per se*, but is dependent on the access of light of a sufficient degree of intensity, and, moreover, that the power is confined to the green parts of the plants. At the same time, whilst recognising, as Priestley had done before him, that the combined action of plants and light on the air was a dephlogisticating process, he did not know, until after its demonstration by Senebier, that the particular form of phlogisticated air which was essential to plants was "fixed air" or carbon dioxide. In fact Ingen-Housz had but a slender knowledge of the chemistry of his day; so much so indeed that he constantly confuses "phlogisticated air" or nitrogen with "fixed air," and attributes the source of the evolved oxygen either to air imprisoned within the leaf, or, in the case of submerged plants, to a metamorphosis of the water itself. I must, however, recall the fact that Ingen-Housz was the first to show that the green parts of plants in the dark, and the roots both in the light and in darkness, vitiate the air in the same way as animals do. On the strength of these experiments he is generally given credit for having first observed the true respiration of plants; but I cannot avoid the conclusion that, in the controversy which ensued on this point between Ingen-Housz and Senebier, the adverse criticisms of the latter were well founded. Whilst not denying that plants in the dark have some mephitic influence on the air around them, Senebier maintained that the greater part of the observed effect was due to a fermentative action set up in the large bulk of leaves which Ingen-Housz employed. Certainly some of the results appear to be largely in excess of those we should now expect to obtain from respiratory processes only.†

Senebier's work falls between the years 1782 and 1800. The fact that he was an early convert to the new ideas

* The view which was taken by Priestley's contemporaries of his position with regard to the discovery of the fundamental facts is well exemplified by the following remarks taken from a paper published by Ingen-Housz in 1784 (*Annales de Physiques*, xxiv., 44):—"C'est à M. Priestley seul que nous devons la grande découverte que les végétaux possèdent le pouvoir de corriger l'air mauvais, et d'améliorer l'air commun; c'est lui qui nous en a ouvert la porte. J'ai été assez constamment attaché à ce beau système, dans le temps que lui-même, par trop peu de prédilection pour ses propres opinions, paroissoit chanceler."

† It is by no means uncommon to find Ingen-Housz put forward as the discoverer of the fixation of carbon by plants from carbon dioxide. This claim is generally based on certain statements made in his essay on the "Food of Plants and the Renovation of the Soil," published in 1796 as an Appendix to the outlines of the fifteenth chapter of the "Proposed General Report from the Board of Agriculture." All that is good and sound in this essay is taken from Senebier's papers without any acknowledgment, but, in appropriating ideas which he evidently understands very imperfectly, he has built up a system of plant economy which is almost unintelligible.

and generalisations of Lavoisier gives his views on plant nutrition far greater precision than those of Priestley and Ingen-Housz. His experiments, for the most part well-devised, proved beyond all doubt that the oxygen disengaged from submerged and insolated plants could not be derived from air contained in the leaf parenchyma, but that it depended on the pre-existence of carbon dioxide, and that its evolution was strictly proportional to the amount of carbon dioxide which the water contained.

Although positive experimental proof was still wanting that aërial plants also derive their carbon from carbon dioxide, Senebier regarded this as extremely probable; but, taking into consideration the small amount of this gas present in the atmosphere, he concluded that it must reach the plant by the roots and leaves entirely in a state of solution in water.

The work of Priestley, Senebier, and Ingen-Housz fortunately attracted the attention of a young chemist of high attainments, who, within a period of less than ten years, did more for the advancement of vegetable physiology than any single observer before or since his time. Théodore de Saussure, the second of that illustrious name, and the son of the famous explorer and natural philosopher, commenced his researches about the year 1796, and in 1804 published his "*Recherches Chimiques sur la Végétation*," a modest little octavo volume of some 300 pages, which must certainly take rank as one of the great classics of scientific literature, and one of the most remarkable books of the century.

De Saussure was a past master in the art of experiment, and the methods which he devised for demonstrating the influence of water, air, and soil on vegetation have been the models on which all such investigations have been conducted ever since. It is indeed very difficult, when reading this masterly essay, to bear in mind that it was not written fifty or sixty years later than the date on its title-page, so essentially modern are its modes of expression and reasoning, and so far is the author in advance of his contemporaries. It is to this work we must refer for the first experimental proof that plants derive at any rate the greater part of their carbon from the surrounding atmosphere. This was shown by De Saussure by a variety of quantitative experiments of a sufficient degree of accuracy to bring out the great leading facts. By making known mixtures of carbon dioxide and air, and submitting them to the action of plants in sunlight, he was able not only to show that the gaseous carbon dioxide was decomposed and the carbon assimilated, but also that the volume of oxygen disengaged was approximately equal to that of the carbon dioxide decomposed.* He also showed that plants growing in the open in moist sand, or in distilled water, and therefore under conditions in which they could not derive any carbon from other than atmospheric sources, not only materially increased in dry weight, but contained much more carbon at the close of the experiment than at the beginning, and had also fixed an appreciable amount of water in the process. That atmospheric carbon dioxide is not only beneficial to plants in sunlight, but is also essential to their very existence, De Saussure proved by introducing an absorbent of this gas into the vessel containing a plant or the branch of a tree rooted naturally in the soil. Under these conditions the portions of the plant enclosed always died. He also ascertained by experiment the increase in dry weight of a sunflower plant during four months of natural growth; and knowing approximately the amount of water transpired during that period, and the maximum amount of solids which this transpired water could possibly introduce into the plant, he calculated that these solids, and the carbon dioxide in solution in the transpiration water, fell far short of accounting for the observed increase in

the dry weight of the plant. This increase must, therefore, be mainly due to the fixation of atmospheric carbon dioxide and water.

It is certainly a remarkable fact that the rigid experimental proofs which De Saussure brought forward in support of his views did not carry conviction to the minds of everyone. His book, however, suffered the fate of many others which have appeared in advance of their time. It is true that De Saussure's doctrines were always kept alive by the advanced physiologists of the French school, such as DeCandolle and Dutrochet; but when Liebig first turned his attention to the subject he found the field in possession of the humus theory of Treviranus, a theory which no longer took any account of the decomposition of carbon dioxide by the leaves, but which derived the whole of the elements of the growing plant from a solution of the soil extract taken up by the roots. We may well say with Sachs, "Nothing can be conceived more deplorable than this theory of nutrition; it would have been bad at the end of the seventeenth century, it is difficult to believe that it could have been published thirty years after De Saussure's work." It is well known how, by the cogency of his reasoning and the force of his genius, Liebig successfully overthrew this heresy, and once more established the doctrine of carbon assimilation as taught by De Saussure; and the accurate work of Boussingault, who, whilst elaborating far more delicate analytical processes than were possessed by chemists in the early days of the century, still in the main used De Saussure's methods, gave the final death-blow to the humus theory, at any rate in the crude form in which it was presented by its originators. No one since that time has questioned the fact that green plants owe the greater part of their carbon to atmospheric sources, and the accumulated experience of two succeeding generations of workers has added proof on proof of the correctness of this great generalisation.

But whilst it cannot be doubted that green plants devoid of parasitic or saprophytic habit derive the principal part of their carbon from the air, is the experimental evidence at present so complete as to exclude all other sources of supply? De Saussure himself certainly left the door open to such a possibility, and although Boussingault held a different view, we find Sachs as late as 1865 maintaining that it is not contrary to the generally accepted theory of assimilation to suppose that there are chlorophyllous plants which decompose carbon dioxide and at the same time absorb ready-formed organic substances whose carbon they utilise in the formation of new organs.

Up to comparatively recently there was little or no experimental evidence to justify this supposition, for the early experiments of De Saussure on the influence of solutions of sugar, and of other organic substances, on growing plants, although very suggestive, were not of a sufficiently precise nature to lead to any conclusions, and we must come down to within fifteen years of the present time for anything like a demonstration that the green organs of plants can, under favourable conditions, build up their tissue from already elaborated carbon compounds just as do the fungi and the non-chlorophyllous plants generally.

The active centres of the decomposition of carbon dioxide in green leaves are the chlorophyll corpuscles or chloroplastids, and the first visible indication of this decomposition is the formation within these chloroplastids of minute granules of starch whose presence can be shown by suitable micro-chemical means. I have elsewhere discussed the question of how far the appearance of this starch is dependent on the pre-existence of other carbohydrates of a simpler constitution, and also the probability that the whole of the products of assimilation do not necessarily pass through the form of starch: this is a subject which need scarcely concern us at the present moment: it is sufficient to draw attention to the main fact that in an assimilating cell the chloroplastids, in the

* Although clearly indicating that no change of volume occurred in the mixture of air and carbon dioxide so treated, his final analytical results show a small apparent evolution of nitrogen. This was due to the eudiometric methods he employed,—methods, it is true, far superior in point of accuracy to those of his predecessors, but still necessarily imperfect.

vast majority of cases, give rise to these minute starch granules, which once more disappear when the plant is placed in darkness, or when the air around it is deprived of carbon dioxide. Now in 1883 Böhm made the interesting discovery that when green leaves are placed in the dark until the starch of their chloroplastids has completely disappeared, there is a reappearance of starch when the cut end of the leaf-stalk is immersed in a solution of cane-sugar and of dextrose, or when the leaf is brought directly in contact with solutions of these substances. He found, in fact, that the elements of the cell which, under ordinary circumstances, manufacture their materials for plant growth by the reduction of carbon dioxide under the influence of sunlight, can, under other conditions, supply their requirements from suitable ready-formed organic substances. These observations of Böhm were fully confirmed two years later by Schimper, and were subsequently much extended by A. Meyer and E. Laurent, who found that fructose, maltose, mannitol, dulcitol, and glycerol could also contribute directly to the nutrition of leaves.

Bokorny, working with *Spirogyra* immersed in dilute solutions, found that starch production in the chlorophyll bodies could be induced by a large number of organic substances, including, amongst many others, asparagin, citric, tartaric, and lactic acids, leucine, tyrosine, and peptone.*

Very much more to the point are the experiments of Acton, made in 1889, and the still more recent work of J. Laurent and of Mazé.

In his experiments on terrestrial plants Acton, after depleting them of starch, immersed the cut branches or roots, as the case might be, in culture fluids containing certain organic substances, and took precautions to prevent any normal assimilation from taking place by depriving the air around the plant of any trace of carbon dioxide. He was not able to show the direct nutritive influence of so large a range of substances as Bokorny had done for *Spirogyra*, but his results leave no room for doubt that several of the carbohydrates, and even glycerin, can be absorbed by the roots, and can contribute to the nutrition of the green parts. Acton tried, amongst other substances, an "extract of natural humus," which was an aqueous solution of the extractives of a light soil which are soluble in dilute alcohol. This extract was found to be effective in producing a small quantity of starch in the leaves, and it evidently contained some substance or substances directly assimilable by the plant.

Apparently without knowing anything of this work of Acton, J. Laurent has recently made a series of experiments on the culture of the maize plant in mineral solutions containing saccharose, glucose, or invert sugar, and in this way has not only obtained, as Acton had done before him, evidence of the active formation of starch in the leaves, but has also found a very notable increase in the dry weight of the plant. Although assimilation of the carbohydrate may under these circumstances go on in darkness, Laurent found that the process was much enhanced when light had access to the plant. Mazé, within the last few months, has obtained even more pronounced effects of this kind.

When all these new facts are taken into consideration, I think they justify what I have already said, that we

* By far the most interesting and important result of Bokorny is the proof he gives that formaldehyde is directly assimilable by *Spirogyra*. His early attempts to show this had been rendered abortive by the highly poisonous nature of this substance. The difficulty was surmounted by using a dilute solution of sodium oxymethylsulphonate, which on warming with water splits up into formaldehyde and acid sodium sulphite. To prevent the unfavourable action of the acid sodium sulphite, dipotassium or disodium phosphate was added to the plant cultures. In such a solution, with rigid exclusion of carbon dioxide, *Spirogyra majuscula* forms starch in its chlorophyll bodies, but the access of light appears to be necessary.

The importance of this experiment is very great in connection with Baeyer's well-known hypothesis that the first act of assimilation is the reduction of carbon dioxide and water to the state of formaldehyde.

ought to demand more direct evidence than is at present available before we accept the view that the majority of chlorophyllous plants take in *the whole* of their carbon from the atmosphere. In the cycle of change which the organic matter of the soil is constantly undergoing under the influence of micro-organisms, it seems by no means improbable that intermediate substances may be formed which in some measure directly contribute to the nutrition of the higher plants, and we must also by no means lose sight of the possible effect, in the same direction, of the symbiotic union of certain fungi with the root extremities of many plants, the Mycorrhizæ, whose functions are still so imperfectly understood. Then, again, we must remember that we have another possible extra-atmospheric source of carbon dioxide in the transpiration water of the plant, which is derived from a soil whose gases may contain 5 per cent or more of carbon dioxide. From the amount of water transpired in a given time, and an application of the law of partial pressures, it may be readily shown that the supply of carbon dioxide to the aerial organs of a plant from this source is by no means negligible.

Before these problems can be attacked for a particular plant with any hope of success it is clear that we must have some means of establishing an accurate debtor and creditor account as between the plant and the surrounding atmosphere, and this account must extend over a sufficiently long period, and allow of an accurate balance being struck with the amount of carbon found in the plant at the end of the experiment.

Up to within a few years ago we had no means of even approximately determining the actual rate at which the assimilatory process goes on in a plant other than that afforded by its increase in weight in a given time. Such experiments, necessarily extending over weeks or months, can, at the best, only give us certain average results, and consequently afford no measure of the activity of assimilation under fixed conditions of insolation. In the year 1814 Sachs, who had for some time been at work on the formation of starch in leaves under the action of sunlight, found that the accumulation of freshly assimilated material in a leaf may, under favourable conditions, go on so rapidly as to give rise to a very appreciable increase of weight in the leaf lamina within the short space of a few hours. By observing at different times of the day the varying dry weight of equal areas of large leaves, Sachs obtained an approximate measure of the rate of the assimilatory process which he could express in terms of actual number of grms. of substance assimilated by a unit area of leaf in unit of time. In this manner he was able to show, for instance, that a sunflower leaf, whilst still attached to the plant, increases in weight when exposed to bright sunshine at the hourly rate of about 1 gm. per square metre of leaf area. In the case of similar leaves detached from the plant, and of course under conditions in which the products of assimilation were entirely accumulated in the leaf, he found an increase in weight of rather more than 1½ gm. per square metre per hour.

I was able to confirm this work of Sachs in the course of an investigation on the Chemistry of Leaves which I made with Dr. G. H. Morris in 1892-93, and there can be no doubt that the variations in the weight of leaves can be used as a fair index of the activity of a leaf in assimilating, but it is not a method which admits of much refinement of accuracy, owing, amongst other things, to the want of perfect symmetry in the leaves as regards thickness and density of the laminæ and to the possible migration of the assimilated material into the larger ribs, which of course cannot be included in the weighings.

It is evident that a far better plan of measuring the rate of assimilation under varying conditions would be the estimation of the actual amount of carbon dioxide entering a given area of the leaf in a certain time, and it was to the perfection of a method of this kind that Mr. Escombe and I first turned our attention.

In all previous attempts to measure the rate of ingress of carbon dioxide, such as those of Corenwinder, and

more recently still of Mr. F. F. Blackman, it has been necessary to use air containing comparatively large quantities of carbon dioxide, amounting to 4 per cent and upwards. Interesting and useful as such experiments undoubtedly are from the point of view from which they were undertaken, we must not lose sight of the fact that such conditions are highly artificial, and very far removed from those under which a plant finds itself in the natural state, where its leaves are bathed with air containing not 4 or 5 per cent but only 0.03 per cent of carbon dioxide. I shall have occasion later on to show how remarkably the rate of intake of carbon dioxide into a plant is influenced by extremely small variations in the tension of that gas, and that on this account no deduction can be drawn as to the rate of assimilation under natural conditions from any experiments in which the air contains even so small an amount of carbon dioxide as 1 per cent.

Before proceeding further in this direction, however, it will be well to consider the amount of carbon dioxide which must enter a leaf in a given time in order to produce an influence on its weight comparable with that indicated by the Sachs method of weighing definite areas. For this purpose I will consider a leaf with which we have made many experiments—that of *Catalpa bignonioides*. It is a very symmetrical leaf and a good assimilator, and since the intake of carbon dioxide takes place only on the under side, the question to which I wish to draw your attention can be stated in a simple manner. When such a leaf is subjected to a modified form of the half-leaf weighing method of Sachs, into the details of which I cannot here enter, it may, under favourable conditions, show an increase in dry weight equal to about 1 gm. per square metre per hour. Since this increase in weight is due almost entirely to the formation of carbohydrates, we can calculate with a close approximation to accuracy the corresponding amount of carbon dioxide. This will of course depend, within certain narrow limits, on the nature of the carbohydrate formed. The formation of a gm. of starch requires 1.628 grms. of carbon dioxide, whilst an equal amount of a $C_6H_{12}O_6$ or a $C_{12}H_{22}O_{11}$ sugar require 1.466 and 1.543 grms. respectively. From the knowledge we possess of the nature of the carbohydrates of the leaf, we are quite sure that the mean of these values—that is, 1.545 grms.—must be very near the truth. This amount corresponds to 784 c.c. of carbon dioxide at normal temperature and pressure, which must represent the volume abstracted by the square metre of leaf surface in one hour from air containing only three parts of carbon dioxide in 10,000, supposing the method of leaf weighing to give correct results. We shall see later on that this intake can be verified by direct estimations; it is equivalent to the total amount of carbon dioxide in a column of air of a cross section equal to that of the leaf, and of a height of 26 decimetres.

The extraordinary power which an assimilating leaf possesses of abstracting carbon dioxide from the air is best shown by comparing it with an equal area of a freely exposed solution of caustic alkali. We have made a very large number of experiments on the rate at which atmospheric carbon dioxide can be taken up by a solution of caustic soda under varying conditions, and have been surprised to find how constant the absorption is. In a moderately still air a square metre of surface of such a freely exposed solution will absorb about 1200 c.c. of carbon dioxide per hour, and this can only be increased to about 1500 c.c. even if the dish is exposed to the full influence of a strong wind out in the open. When the surface of the liquid is constantly renewed during the experiment by means of a mechanical stirrer, the rate of absorption is not sensibly affected, providing the agitation does not appreciably increase the surface area, and considerable variations in the strength of the alkaline solution are also without any effect. On the other hand, slight variations in the tension of the carbon dioxide of the air have a marked influence on the rate of absorption, and in order to study this point we have constructed an

apparatus which allows us to pass over an absorptive surface of liquid a current of air in a stratum of known thickness, and with a known average velocity.

By introducing definite amounts of carbon dioxide into this stream of air we have been able to determine the influence of its tension on the rate of absorption. At present we have only employed air containing amounts varying from 0.8 to 13 parts per 10,000; that is to say, from about one-quarter to a little more than four times the amount contained in normal air. Within these limits, and probably beyond them, the rate of absorption by the alkaline surface is strictly proportional to the tension of the carbon dioxide in the air current. I shall have occasion to show later on that the same rule holds good with regard to an assimilating leaf, and that in this case also, within certain limits, the intake of the gas is proportional to its tension.

The fact which I wish more particularly to bring out in these comparisons is that a leaf surface which is assimilating at the rate of 1 gm. of carbohydrate per square metre per hour is absorbing atmospheric carbon dioxide *more than half as fast as the same surface would do if wetted with a constantly renewed film of a strong solution of caustic alkali.*

From what I have just said about the influence of tension on the absorption of carbon dioxide by an assimilating leaf, it is clear that any attempts to determine by direct means the natural intake of that gas during assimilation must be made with *ordinary* air, and that such experiments can only be carried out on a comparatively large scale. We had in the first instance to devise an apparatus which would rapidly and completely absorb the whole of the carbon dioxide from a stream of air passing through it at the rate of from 100 to 200 litres per hour, and at the same time admit of an extremely accurate determination of the absorbed carbon dioxide.

The absorbing apparatus which we finally adopted is a modification of one used by Reiset in his estimations of the carbon dioxide of the atmosphere. It consists essentially of a glass tube 50 c.m. long, fixed vertically in a wide-mouthed glass vessel furnished with a second aperture and a tubulure. The height of the vertical tube is invariable, but its width is regulated according to the amount of air required to be drawn through the apparatus in a given time. The bottom of this tube is closed with a platinum or silver plate pierced with a large number of very small holes, and two other similar perforated plates are inserted in the tube at certain intervals. The upper part of the tube is put in connection with an aspirating water-pump, and the absorbing liquid is placed in the lower glass vessel, whose second tubulure is connected with the supply of air in which the carbon dioxide has to be determined. When the aspirator is started the liquid is first drawn up into the vertical tube, and the air then follows through the perforated plates which act as "scrubbers." Reiset, in his work, used baryta-water as the absorbent, an aliquot part of which was titrated before and after the experiment, the changes in the volume of the liquid being corrected for by certain devices which I need not describe.

The efficiency of the apparatus as a complete absorber of atmospheric carbon dioxide leaves nothing to be desired, but in dealing with large quantities of baryta solution, amounting to 400 c.c. or more, the errors due to inaccurate titrations, or to over or under estimation of the volume changes, are all thrown on the final result, of which they may form a considerable part. We have consequently altogether discarded the use of baryta as an absorbent in favour of caustic soda. The carbonate is estimated by a double titration process, suggested a few years ago by Hart, and we have succeeded in so far improving this method that there is no difficulty in determining in 100 c.c. of the alkaline solution an amount of carbonate corresponding to $\frac{1}{10}$ c.c. of carbon dioxide.

There is practically no limit to the amount of air which can be passed through an absorbing apparatus such as I have described, and one of very moderate dimensions will

allow from 100 to 150 litres per hour to pass with perfect safety. Larger amounts can be dealt with either by increasing the size of the apparatus or by using several smaller ones arranged in parallel.

With proper precautions, determinations can certainly be made to within 0.02 part of carbon dioxide in 10,000 of air, so that with an apparatus of this kind it is possible to estimate the intake of carbon dioxide into a leaf or plant from ordinary atmospheric air, and to keep a sufficiently rapid stream of air passing over the leaf to maintain the tension of the carbon dioxide only slightly below the normal amount.

The air is measured by carefully standardised meters, reading to about 20 c.c.; and since the amounts of air aspirated vary from 100 to 900 litres or more, there are practically no errors of measurement. The tension at which the air passes through the absorption apparatus is measured by a manometer, and all the volumes are reduced to standard temperature and pressure.

All such experiments of course necessitate not only a determination of the carbon dioxide in the air which has passed over the leaf or plant, but also a simultaneous determination of the carbon dioxide in the ordinary air used. The accumulation of these air determinations clearly shows that the ordinary statements of our text-books as to the amount of carbon dioxide and its limits of variation are altogether misleading.

In our experiments the air was in all cases taken from a height of 4 feet 6 inches from the ground, the amounts aspirated varying from 100 to 500 litres.

In the month of July, 1898, the minimum amount of carbon dioxide found was 2.71 parts per 10,000 of air, and the maximum 2.86. During the winter months, when the ground was almost bare of vegetation, it rose to from 3.00 to 3.23 parts per 10,000; and on one foggy day, March 16, 1899, after a whole week of similar weather, we found the very exceptional amount of 3.62. As a rule we may take it that the amount of carbon dioxide in the atmosphere during the period of greatest plant growth rarely falls short of 2.7 parts per 10,000, and rarely exceeds 3.0 parts, with an average of about 2.85. These numbers come very close to the determinations of Reiset, and of Müntz and Aubin, and agree also fairly well with the Montsouris determinations.

(To be continued).

PROPOSED INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS.*

By Professor F. W. CLARKE.

(Letter to Professor W. A. TILDEN).

Washington, D.C., July 19, 1899.

DEAR SIR,—In response to your letter of June 8, I take pleasure in sending you a statement of my views relative to the proposed International Committee upon Atomic Weights. The suggestions which I have to offer are, however, only my own individual opinions, and are not to be regarded as representing any organisation, or as based upon any definite programme. Still, they may serve as a basis for discussion, and so help to clear a way for progress.

Every chemist who has studied, with any closeness, the determination of atomic weights, has noticed the discordance which exists among the published tables. In many text-books and works of reference tables are given which seem to have been edited with a pair of scissors and a paste-pot, and which show about as much critical acumen in their making up as those useful implements could furnish. Not only are obsolete values found persisting, but values are given which are inconsistent among them-

selves; and occasionally there is evidence of the most pitiable confusion as to the fundamental standards of reference. One table is based upon the standard of oxygen as 16; another upon oxygen as 15.88, and still others upon the wholly erroneous ratio of 15.96. In one and the same table these several standards may simultaneously appear, one atomic weight being referred to one, and another to another; the compiler being quite unconscious of the discrepancy. Tables of atomic weights which were good ten years ago reappear frequently in books of to-day, with no hint that any changes have occurred in any of the data.

In order to remedy, at least in part, this unnecessary confusion in our fundamental constants, the American Chemical Society in 1892 requested me to prepare an annual report upon atomic weights. Each year since I have submitted to the Society such a report (six in all), giving a summary of the determinations made, and a table of values brought down to the date of publication. So far as it went, the work seems to have been useful; but it did not go far enough, and it carried only the authority which might attach to the opinions of a single individual. More criticism, more comparison of views among chemists, was evidently desirable; and the movement in favour of international action seems to be a movement in the proper direction.

In 1898 the subject was taken up independently by the German Chemical Society, which appointed a committee consisting of Landolt, Ostwald, and Seubert. This committee in due time reported a table of atomic weights, recommending the adoption of $O=16$ as the standard of reference, and suggested that like committees might well be appointed by other societies for purposes of co-operation. Acting upon that suggestion, the American Chemical Society, at its last general meeting, appointed a committee consisting of F. W. Clarke, J. W. Mallet, E. W. Morley, T. W. Richards, and Edgar F. Smith; and that committee has already begun correspondence with the English and German organisations. A number of local societies in various parts of Europe have recommended the use of the table put forth by the German Committee; but a full conference of all the parties at interest is yet to be held. Probably an effort will be made to discuss the atomic weight question at the Congress of Chemists in Paris next year; but this proposition is so far only a matter under consideration. At all events, a general international committee might then be most readily brought together; and its recommendations would certainly carry much weight.

What, now, could such a committee accomplish? In what directions should its influence be exerted? These are questions to be answered beforehand, for upon the answers the expediency of definite action must depend. Unless we have a reasonable expectation that something useful can be done, it is not worth while to go any further.

Two lines of discussion for the proposed committee are self-evident:—First, a discussion of the ultimate standard of reference, whether it shall be $O=16$ or $H=1$, and upon this question there are legitimate differences of opinion; secondly, a discussion of the existing data, in order to determine the most probable values for the atomic weights, and to get some insight into their relative accuracy. This involves the preparation of a table of atomic weights for practical use, in which some indication shall be given as to the trustworthiness of the individual values. Which figures have been well determined, and which need correction, should be clearly shown, and in that way future investigation would be stimulated. Such a table would call for revision from time to time, perhaps annually, and for this reason the committee should be made a permanent body, to act either by meeting or by correspondence, according to circumstances. Only an international committee could expect to have its findings generally accepted.

Up to this point the work proposed for the committee has already been done, with more or less thoroughness,

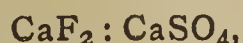
* Read before the British Association (Section B), Dover Meeting, 1899.

by the German committee, by Professor Richards, and by myself; so that the ground is pretty well cleared, and the field of action can be seen. But still more is desirable; and just here, I believe, the task of the proposed committee may become most important. Having ascertained the weak points in our system of atomic weights, the next thing to do is to have them strengthened; and to this end the combined influence of a body of trained experts might well be exerted. At present, all research in this field of investigation is individual, and consequently the more obvious problems are simultaneously attacked by sometimes several independent workers, while other equally important questions are entirely neglected. A division of the field of labour, and co-operation in research, might easily be brought about; not by any exercise of authority on the part of the committee, but but by mutual consent of the investigators, working in conference, and aided by the suggestions which the international body might develop. In short, the committee could not order, but it might persuade; and in this direction its influence ought to be decidedly beneficial. Even if it did no more than to point out the essential problems to be solved, it would fully justify its existence.

There is one more general problem which the proposed committee should consider: that of methods. What are the best experimental methods for the determination of atomic weight ratios, and how shall the data be handled mathematically? On each division of this question there is something to be said. The existing methods, the methods which are commonly employed, are somewhat conventional in their character, and need exhaustive scrutiny. They are not sufficiently varied in their details to eliminate all danger of constant or cumulative errors, and new lines of attack, new points of view, ought to be considered and developed.

At present, the data relative to atomic weights are treated like successive links in a series of chains, each link to be considered separately; while in reality they form an interlacing network of interdependent quantities which should be discussed in some broadly general way.

To illustrate my meaning, let us consider a specific ratio,—



which has been repeatedly measured in order to determine the atomic weight of fluorine. In this case a series of measurements is made, involving of necessity some error which may be great or small. From these data the atomic weight in question is computed, with the assumption that the atomic weights of calcium and sulphur are known. But these antecedent values are themselves in error by small but unknown amounts, and these errors are superimposed upon the experimental error of the ratio itself, so that all three appear in the final result of the calculation. The errors may be compensatory in part, or they may be cumulative; and which is the case we cannot certainly know. In a proper reduction of the data the ratio should contribute to our knowledge of all three of the atomic weights represented, and its error should be distributed among them instead of being piled, with others, upon one. That is, the ratio should not be discussed by itself, but should be combined with other ratios in such a manner that several related atomic weights might be determined simultaneously. This, I believe, will be the method of the future; and ultimately all trustworthy evidence, concerning all atomic weights, will be put into one set of normal equations with simultaneous solution for all. First, the experimental errors will be made as small as possible; after that they will be so uniformly distributed as to become inappreciable. For this procedure the mathematical method is well known, but the existing data are too incomplete for its present application. The final reductions will not be possible for many years to come. Work, comparable with that of Stas and Morley, needs to be done for all the chemical elements, and done with a broad purpose in view; after that, the

mathematician can contribute his share to the solution of the general problem.

It is greatly to be hoped that at some future time some of the great laboratories may undertake systematic work of the kind I have indicated. The fundamental constants of chemistry are surely of equal importance with the value of the ohm, the form of the earth, or the solar parallax; and institutions like the Reichsanstalt in Berlin, the International Bureau of Weights and Measures at Paris, or the Davy-Faraday Laboratory of the Royal Institution, might well contribute to their determination. In this direction an international committee could exert an influence far beyond that of any individual, or even of any one society, but the problems at issue must first be clearly understood and formulated. To clear the ground, to arouse interest, and to stimulate systematic research, are important functions of the proposed body.

Yours very truly,

F. W. CLARKE.

ATOMIC WEIGHTS.*

By Professor W. A. TILDEN, F.R.S.

THE question of atomic weights has two aspects, the theoretical and the practical. For the purposes of theory we require to know the relative values of the atomic weights of all the elements with the utmost possible accuracy, with the object chiefly of explaining observed relations and discovering new ones. The true significance of the periodic scheme of arrangement will never be discovered till the atomic weights of a much larger number of elements are known more correctly than at present. And the employment of numbers which only roughly approximate to the true values for the atomic weights has led in the past to a large amount of speculation and discussion, of which nearly the whole is fruitless, because of necessity successive hypotheses have had to be put aside as knowledge of the subject has advanced, and numbers less inaccurate have been gradually substituted. This is true not only of such crude hypotheses as that of Prout, but of ideas proposed in more recent times concerning the relations of the several series in Mendeleeff's table.

Other questions have arisen, such as the possibility of the variation of the atomic weights within certain limits, but they only serve to illustrate the extreme difficulty of the subject in its present position; for while the facts are about equally well known to all chemists who have studied it, they have led some to consider variation possible, while others upon the same evidence are convinced that it is impossible. Unfortunately the settlement of such questions is still far off, for the complete series of determinations of all the elements made with a degree of accuracy comparable with that which has made the work of Stas famous is not to be expected in the present generation.

Another subject which has been re-opened by the action of the distinguished Committee of the German Chemical Society relates to the unit to be adopted. The practice which has prevailed universally since the time of Berzelius—that is, for nearly three-quarters of a century—of expressing the atomic weights in terms of hydrogen ($H=1$) is now abandoned by the Committee in favour of the new scale, in which oxygen is the standard and $O=16$. The considerations which have influenced the several members of the Committee are chiefly three, namely, first, the uncertainty still supposed to attach to the ratio $H:O$, though this is now as accurately known as it is likely to be; secondly, the fact that the atomic weights of many elements may be deduced directly from the composition of their compounds with oxygen, but less frequently from compounds with hydrogen; thirdly and chiefly, because

* Read before the British Association (Section B), Dover Meeting, 1899.

the oxygen scale brings many atomic weights very near to whole numbers. It is evident that this consideration is one which concerns alike the analyst, the student, and the investigator in every analytical operation, and in all circumstances which do not involve the discussion of the numerical interrelations of the atomic weights. For that purpose the $H=1$ scale will always be preferable, until an element is discovered having a smaller atomic weight than hydrogen, and of that there is at present no indication so far as terrestrial chemistry is concerned.

On the whole, the proposal of the German Chemical Society is probably the best solution of the difficulty. The scale in which $O=16$, however, implies the value 1.01, approximately, for hydrogen, and though it is true that for common analytical use the neglect to recognise this value will not lead to very serious consequences, it must be remembered that an appreciable error will be evolved in expressing the composition of compounds which are comparatively rich in hydrogen, such as the chief hydrocarbons and their derivatives. For C_5H_{12} , for example, the percentage of hydrogen is 16.66 or 16.80, according to the value assigned to the atomic weight of hydrogen.

But supposing the $O=16$ scale to be generally adopted, it is still highly desirable that there should be an understanding among the several Chemical Societies, and if possible among the members of these societies, as to the numbers to be chosen for ordinary use. Are we to use 27.1 for Al, 137.4 for Ba, 208.5 for Bi, 79.96 for Br, 35.45 for Cl, 52.1 for Cr, 126.85 for I, 206.9 for Pb, 24.36 for Mg, 200.3 for Hg, 14.04 for N, 194.8 for Pt, 39.15 for K, 23.05 for Na, 32.06 for S, &c., instead of the nearest whole numbers as has been customary in all these cases, with one exception, namely, chlorine? The temptation will be great, especially when we become aware that in the majority of cases the error introduced will be less than the ordinary experimental error. The example of platinum at once presents itself, without concerning yourselves about the special value for this element used by the potash makers for reasons of their own. But comparing the result of employing the old rounded off numbers with that of using the more exact values calculated on the $O=16$ scale, it is interesting to see how little is the effect on the percentage composition of potassium platino-chloride deduced from the formula.

Percentages calculated from—			
	K=39.15, Pt=194.8, Cl=35.45.	K=39, Pt=195, Cl=35.5.	Difference.
Potassium ..	16.118	16.049	0.069
Platinum ..	40.099	40.123	0.024
Chlorine ..	43.783	43.827	0.044
	100.000	99.999	

There are some chemists to whom anything short of scientific accuracy is distasteful. It would be interesting to know whether in their daily work they use, for example, the number 14.04, instead of 14 for nitrogen, and what is the extent of experimental error they admit in analyses of nitrates or ammonia salts, of nitro compounds, or of organic matters by Kjeldahl, or any other recognised process. The composition of nitro-benzene may be used as an illustration. The percentage of N derived from the formula when $C=12$, $H=1$, $N=14$, $O=16$ is 11.38; while if $C=12$, $H=1.01$, $N=14.04$, and $O=16$, the result is 11.40, a difference of 0.02 per cent.

It is also usually forgotten that the values arrived at in all the best determinations of atomic weights are obtained under conditions which cannot be observed in daily laboratory practice, the weights, for example, being usually reduced to a vacuum standard. Hence the adoption of the numbers regarded as the most exact does not necessarily contribute to the exactness of ordinary analytical operations, however carefully performed.

A little common sense is required in all such matters, but it should be the common sense of the chemical world,

and not the diverse fancies of individuals, and uniformity of practice would tend greatly to the general convenience. The only chance of arriving at such uniformity is to submit the question to discussion first at such meetings as those of the British Association and the Chemical Society, and subsequently at an international gathering such as it is proposed to hold in Paris next year. On such grounds I support cordially the chief proposals brought forward in the communication from Professor F. W. Clarke.

ON THE CHLOROBROMIDES OF LEAD.

By V. THOMAS.

In previous articles I have shown that chloride of lead was capable of giving with the iodide a well defined mixed salt, $PbICl$ (*Bull. Soc. Chim.*, vol. xix., p. 488, 1898), and that the bromide treated in the same manner also led to the formation of a very homogeneous crystallised substance corresponding to the formula $3PbCl_2, PbBr_2$. The attack of the chloriodised compound by peroxide of nitrogen is effected with the greatest facility, and thus allows the fact of its chemical existence to be easily demonstrated. The application of this method to the study of the chlorobromide does not lead to any result; the peroxide of nitrogen is not, in fact, able to displace the bromised quantitatively even at a high temperature.

Bromide and chloride of lead, both crystallise in the same system, and the formation of mixed isomorphous salts containing variable proportions of chlorine and of bromine might here occur, and cause some doubt as to the chemical personality of the compound $3PbCl_2, PbBr_2$. Thus, following my researches, I carried out with great care the determinations of the halogens in the products deposited at various temperatures.

This determination was carried out on the bodies deposited after the preparation of $3PbCl_2, PbBr_2$ at every 10° , from 60° to about 20° . Further, by the aid of titrated solutions I was able to constantly follow the variation in composition of the deposits between known temperatures.

The following are the results of some quantitative estimations:—

Part deposited below 60° .	Cl per cent.	Br per cent.
Between 60° and 50°	17.82	13.42
„ 50° „ 40°	17.58	13.51
„ 40° „ 30°	17.90	13.29
„ 30° „ 20°	17.73	13.43

Theory requires for $3PbCl_2, PbBr_2$, $Cl=17.79$, $Br=13.37\%$. To follow the phenomenon between any two temperatures, such as 50° to 40° for example, we take at each intermediate degree of temperature a certain quantity of the substance deposited; this is then dissolved in water containing a small quantity of nitric acid; a known quantity of nitrate of silver (more than enough to precipitate all the halogens) is added to the solution; the excess of nitrate of silver is then titrated by means of sulphocyanide. In following this method, which is fairly rapid, we are able to see that the total amount of halogens contained in the precipitate is the same at each instant. If the compound $3PbCl_2, PbBr_2$ had not a definite chemical existence, but represented only an isomorphous mixture of the chloride and the bromide, the chemical composition of such a mixture, between sufficiently wide degrees of temperature, should oscillate between two limits of composition. It is the constancy of the composition of the product contained which causes me to be of the opinion that this chlorobromide has a definite composition.

I was able to obtain another mixed compound of chloride and bromide of lead by using the property possessed by bromine of displacing iodine from most of its metallic compounds. Thus in treating the chloriodide of lead

PbICl by a current of bromine this latter takes the place of the iodine, giving the chlorobromide PbBrCl. This substitution is further effected at only a slightly elevated temperature, and the chlorobromide thus obtained retains the form of the chloriodide which has served for its preparation. When slightly heated it melts, giving a liquid having a pale yellow colour, and which on cooling takes the form of a crystalline mass.

The synthetical and analytical results are as follows:—

I. *Synthesis.*— $\text{PbICl} + \text{Br} = \text{PbBrCl} + \text{I}$.

	Found.	Calculated.
Loss of weight	12.9	12.7
Iodine disengaged	34.01	34.46

II. *Estimation of the Lead and the Halogens in PbBrCl.*

	Found.	Calculated.
Pb	63.97	64.07
Br	25.23	24.88
Cl	10.92	11.05

The properties of this chlorobromide are the same as those of the compound previously described.

It does not appear to be affected by light; water dissolves it with decomposition; hydrochloric and hydrobromic acids act in the same manner, giving the corresponding haloid salts; nitric acid, either pure or charged with nitrous vapours, also attacks it very rapidly.

Glacial acetic acid does not dissolve it; alcohol at 95° only dissolves it in very small quantities, even when boiling; chloroform has no action at all.

When treated with fuming hydriodic acid it gives iodide of lead; after a sufficient time the transformation is complete.

In a forthcoming note I shall describe the double compounds of bromide and iodide of lead.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 11.

ON THE MANUFACTURE OF NITRITE OF SODA.

By M. A. DARBON.

DETAILS of the manufacture of nitrite of soda are very scarce in chemical literature; it will therefore be of interest to briefly describe the production of this substance, which is now very widely used in the dyeing industry. The raw material used in its manufacture consists of purified Chili saltpetre, and although the presence of sodic chloride may interfere with the value of the nitrite, the re-crystallisation of commercial saltpetre, with a view to the elimination of the sodic chloride, is not practised, as the expenses connected with the operation would be too great.

The saltpetre is melted in large cast-iron vessels, an operation which includes the evaporation of the hygroscopic water, and the decomposition of a part of the iodides and iodates which accompany the saltpetre. At 310° saltpetre begins to fuse, and before adding the lead necessary for its decomposition the temperature is raised to about 400—420°.

The lead should be as pure as possible, as the presence of small quantities of other metals might cause the decrepitation of the whole charge; it is, above all, antimony which is the most to be feared; the lead used must be in thin sheets. About 280 parts of lead are necessary for 100 parts of saltpetre. As soon as the melted saltpetre has reached the desired temperature the necessary quantity of lead is gradually added; at the same time the whole must be kept constantly stirred so as to obtain a very intimate mixture. It is necessary to carefully watch that the charge does not become too strongly heated, for fear the vessel might be pierced; in case of emergency, to prevent such an accident, a quantity of cold saltpetre

must be added, or the fire withdrawn. When all the lead has been added the stirring must still be kept up for some time, and the melted mass is then removed by means of a large cast-iron ladle. It is then run in the form of fine threads into cold water in which its solution is helped by constant stirring. The decomposition of the saltpetre by the lead at 420—500° has the effect of producing, besides the nitrite, about 1 per cent of caustic soda, which dissolves a certain quantity of the oxide of lead formed; this latter should also be removed. This is generally effected by neutralising with nitric acid; in this manner saltpetre is re-formed, while the oxide of lead is precipitated in the state of insoluble hydroxide. We may also use nitrate of lead or sulphuric acid for neutralising the solution; sulphuric acid is preferable on account of its low price, but we then obtain sulphate of soda, which is deposited in the concentrating vessels in the form of the anhydrous salt. We thus have in aqueous solution nitrite, undecomposed saltpetre, caustic soda holding oxide of lead in solution, and the soluble impurities of the saltpetre, such as chloride of sodium, &c. The insoluble residue consists of oxide of lead, a very small quantity of metallic lead, which has escaped oxidation, and a certain proportion of peroxide of lead. The solution diluted to about 6—8° Baumé is neutralised with nitric acid (or dilute sulphuric acid, or again with a solution of nitrate of lead); the oxide of lead in solution is precipitated, and the addition of the acid is continued as long as a precipitate is formed.

We may here correct an error which has slipped into most treatises on chemistry; most authors state that nitrite of sodium has an alkaline reaction, but this is not the case—the pure nitrite is absolutely neutral.

The neutralised solution separated from the insoluble residue by any convenient method is concentrated in cast-iron basins until it reaches 42—45° Baumé when warm.

The insoluble residue is thrown on a large filter of coarse material, such as sacking, washed with warm water, and the wash-waters added to the principal solution. The residuary oxide of lead is capable of various applications, which will be dealt with directly. The concentrated solutions are added together in cast-iron vats and left to crystallise; if the crystals thus obtained are not pure they must be re-dissolved and re-crystallised. The pure crystals are separated in a centrifugal machine, washed, dried, and packed.

The desiccation takes place in an oven, the temperature of which is carried to about 50°, and the crystals are packed in cylinders of double thicknesses of parchment paper.

The residuary oxide of lead may be either melted and cast as it is, reduced to the metallic state, or transformed into minium; it can also be used for the preparation of white-lead, of nitrate, acetate, or other plumbic compounds.

The analysis of the nitrite is generally made with a titrated solution of permanganate of potassium. By dissolving 9.594 grms. of permanganate in 1 litre of water we obtain a solution, each c.c. of which is equal to 1 centigram. of nitrite of sodium.

The analysis is carried out in the following manner:—A known quantity of the nitrite is rapidly weighed and dissolved in an Erlenmeyer flask of 150—200 c.c. capacity with about 80 c.c. of water. To this solution are added a few c.c. of dilute sulphuric acid (1:4), and it is then titrated. When the colouration begins to disappear with difficulty, a fresh quantity of sulphuric acid, much stronger than the last, is added, as there is now no longer any danger of nitrous acid escaping. The addition of the permanganate is continued drop by drop until the rose tint is permanent for about a quarter of an hour.

To hasten the final reaction the solution may be heated towards the end of the operation to 30—40°. The analysis of the melted mass is carried out in the same manner as is that of the oxide of lead to see if the washing was thoroughly done.—*Chemiker Zeitung*, 1899, p. 173.

CORRESPONDENCE.

DETERMINATION OF CARBON IN
IRON AND STEEL WITHOUT COMBUSTION
APPARATUS.*To the Editor of the Chemical News.*

SIR,—May I call the attention of those interested to a few points in the process Mr. Dougherty has described (CHEM. NEWS, lxxx., 121) for the estimation of carbon in steel?

The fact that the method is not so novel as seems to be imagined might well be overlooked if it were not that the claims made for it are occasionally exaggerated, and the data for the calculation is at variance with that of other experimenters.

Papers on similar lines, usually claiming the process as an approximate one, must be known to most chemists actually engaged in iron analysis; the statement, however, that "the method seems to be fully equal to the elaborate standard combustion process, and has the advantage of being simpler and quicker, with fewer possible sources of error," may well be taken exception to. The greater simplicity may be admitted; the greater rapidity is less obvious, since both processes are alike except in the manner of burning the carbon; the greater freedom from error must be emphatically denied, because, apart from errors inherent in the process, the presence of the not uncommon elements chromium and tungsten would invalidate it altogether.

I can hardly imagine anyone at all familiar with the literature of iron and steel analysis assuming that the residue from the treatment with the double copper salt solution was pure carbon. Mr. Dougherty's countryman, Blair—who by the way calls attention to a similar process in his *Chemical Analysis of Iron*—finds the carbonaceous residue to be $(C_{50}H_{21}ClO_{15})_3NO_2$. Schützenberger and Bourgeois reckon it to be $C_{11}H_6O_3$, and Zaboudsky—after liberating the carbon by solutions of copper or silver, or mercury salts—writes its composition $C_{12}H_6O_3$, and prepares organic derivatives therefrom. Calculated from either Schützenberger's or Zaboudsky's formula, the percentage of carbon is over 70. Blair says the residue contains about 70 per cent of carbon. Mr. Dougherty's figure is 67.5.

In one respect Mr. Dougherty's procedure is, so far as I am aware, certainly original. The carbonaceous residue is washed four times with hot nitric acid. Zaboudsky says the residue is soluble in warm nitric acid, and this is true, in a lesser degree, even at the dilution used by Mr. Dougherty.

Boussingault, who seems to have initiated the indirect estimation of carbon on the above principle, determines both combined carbon and graphite in the residue from the same example. (See CHEM. NEWS, 1870, xxii., 317).—I am, &c.,

HARRY BREARLEY.

Addendum.—The vision conjured up by the phrase "the elaborate standard combustion process" will generally accord with the descriptions given of it in text-books, which by no means truly represent the unadorned process as carried out in a busy iron works' laboratory. Except that the apparatus is rather bulky, there is nothing elaborate about the dry combustion process. It is merely a heated tube suitably packed, having a KHO wash-bottle at one end, and a $CaCl_2$ drying tube and weighed absorption bulb at the other. A supply of oxygen is not indispensable, and the boats may be taken in and out of the hot tube. Thus in a stream of air the dried carbonaceous residues are successively burnt each twenty minutes. A similar procedure is, I believe, practised extensively where all varieties of steel are analysed, and the agree-

ment with the most carefully conducted combustions is remarkable.

Some time ago there was occasion to determine whether the sometime unavoidable rapid evolution of gas during direct combustions with lead peroxide was more than the KHO bulbs and the attached $CaCl_2$ tube could cope with; the following experiments were therefore made:—

An aspirator, having constant suction, drew $2\frac{1}{2}$ litres of air through the furnace and a KHO bulb in eight minutes. The $CaCl_2$ tube belonging to the bulb held only 2 inches of $CaCl_2$, yet the loss through imperfect dehydration was only 0.00175 gm. The same bulb was attached to the furnace, the carbonaceous residue from 5 grms. of steel was kept in the tube at full red heat for five minutes, then the current of air passed at the same rate as before. The increased weight of the bulb calculated to 1.17 per cent carbon; numerous previous determinations have fixed the percentage at 1.18. Thus the absorption of the CO_2 was nearly perfect, although the gas passed about ten times faster than text-book rate.

Taken all in all, and particularly when steels containing special elements are daily dealt with, there are few processes that combine speed and accuracy more satisfactorily than dissolving in a copper solution by means of a mechanical shaker and dry combustion of the residue: certainly Dougherty's is not one.

September 11, 1899.

THE 32 EQUIVALENT AND ITS RELATION
TO THE PERCENTAGE OF AVAILABLE SODA
IN CAUSTIC SODA.*To the Editor of the Chemical News.*

SIR,—I have been out of Chicago since writing my last letter, and have only recently had the opportunity of reading Mr. Pattinson's letter dated May 24th replying to mine.

With regard to Mr. Pattinson's opening statement, I would say I do not claim to have quoted his exact words.

Mr. Pattinson's criticisms upon my method of calculation appear to me justifiable, and unless an acid is truly normal the principle of equivalents cannot be applied to it.

It would therefore appear that, as the "Tyne test" was originated by the assumption that the atomic weight of sodium was 24, it will be necessary to prepare an acid which will saturate 41 grms. NaHO per litre in order to get correct results for caustic soda on this basis. Of course, an arbitrary calculation might be made with the acid prepared to give correct results with sodium carbonate.—I am, &c.,

H. A. HOOPER.

Chicago, Ill., U.S.A., August 5, 1899.

The South Western Polytechnic.—The operations of this Institute are divided into two distinct portions:—Day Classes for both Men and Women, and Evening Classes. The latter offer to artisans and others engaged in technical and commercial industries the means of instruction in Applied Science and Art. The Institute is lighted throughout by electricity, and provided with well-equipped Mechanical, Electrical, Physical, Chemical, and Biological Laboratories, with Art and Photographic Studios, and with Workshops. It is directed by a Governing Body, consisting of representatives of the City Parochial Charities, the London County Council, the London School Board, and the Chelsea Vestry. The whole is under the supervision of the Principal, Prof. Herbert Tomlinson, B.A., F.R.S., assisted by the many Professors, Lecturers, Demonstrators, and Instructors, which the extensive list of studies necessitates. The new Session commences on Monday, September 25th,

CHEMICAL NOTICES FROM FOREIGN SOURCES

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 8, August 21, 1899.

Decomposition of Monomanganous Phosphate at 0° and at 100°.—Georges Viard.—It has been known for some time that monomanganous phosphate, $(\text{PO}_4)_2\text{MnH}_4 + 2\text{H}_2\text{O}$, is decomposed both by hot and cold water. Cold water gives a crystalline precipitate of di-manganous phosphate, $(\text{PO}_4)_2\text{Mn}_2\text{H}_2 + 6\text{H}_2\text{O}$, whilst hot water gives a crystalline precipitate, $(\text{PO}_4)_2\text{Mn}_2\text{H}_2 + (\text{PO}_4)_2\text{Mn}_3 + 4\text{H}_2\text{O}$, which is intermediate between the di- and tri-manganous phosphate, and sometimes called ditrimanganous phosphate. The author has studied these reactions quantitatively. The method employed is that of Gibbs, which in this case is particularly useful, since the liquid always contains more than double the quantity of phosphoric acid necessary to form ammonia-manganous phosphate. The results are shown on a curve.

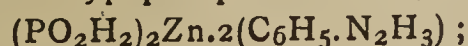
Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxi., No. 7.

On the Hydrosulphites of Ammonium.—Maurice Prud'homme.—Already inserted in full.

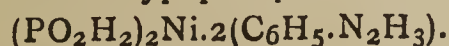
On a New Mineral: Carnotite.—C. Friedel and E. Cumenge.—Already inserted in full.

Action of Acetate of Lead in Acetic Solution on Chloride of Benzylidene and Chloride of Benzenyl.—F. Bodroux.—The author has endeavoured to prepare acetate of benzylidene by a similar method to that used for preparing acetic ethers. For this purpose he dissolves 35 grammes of litharge in 80 grms. of acetic acid, and having added 20 grms. of chloride of benzylidene he carried the whole to boiling-point. A violent reaction commenced immediately; the flame was then withdrawn, but the reaction continued for some little time. When it ceased, he boiled up again for ten minutes; then, after cooling, he filtered and drove off about three-quarters of the acetic acid by distillation. The residue, treated with a cold dilute solution of potash, gave about 20 grms. of an oily liquid, which, after decanting and washing with water, was dissolved in ether; the dried solution was allowed to stand. On evaporation, the product of the reaction, which possessed a strong smell of bitter almonds, crystallised slowly and partially in colourless plates, melting, without decomposition, at 45–46°.

Phenylhydrazinic Compounds of Metallic Hyposulphites, Hyposulphates, and Hypophosphites.—J. Moitessier.—Phenylhydrazine forms—the same as does ammonia—crystallised compounds with the hyposulphites, hyposulphates, and the hypophosphites of the metals of the magnesium series. The author here describes the preparation and properties of phenylhydrazinic hyposulphite of cadmium, $\text{S}_2\text{O}_3\text{Cd} \cdot 2(\text{C}_6\text{H}_5 \cdot \text{N}_2\text{H}_3)$; phenylhydrazinic manganous hyposulphate, $\text{S}_2\text{O}_6\text{Mn} \cdot 5(\text{C}_6\text{H}_5 \cdot \text{N}_2\text{H}_3)$; phenylhydrazinic hypophosphite of zinc,—



and phenylhydrazinic hypophosphite of nickel,—



Other salts of the metals of the magnesium series, such as the selenates, pyrophosphates, and the borates, also give phenylhydrazinic compounds. Further, by working at a low temperature and in alcoholic solution, the author has obtained a compound of phenylhydrazine and nitrate of silver; it is, however, very unstable at the ordinary temperature.

MISCELLANEOUS

British Association for the Advancement of Science.—The following are the names of the Officers and Committee of Section B (Chemical Science) at the Dover Meeting of the British Association:—

President—Horace T. Brown, LL.D., F.R.S.

Vice-Presidents—Prof. H. E. Armstrong, F.R.S.; Prof. P. Frankland, F.R.S.; Prof. A. Ladenburg; Prof. F. R. Japp, F.R.S.; Prof. R. Fittig.

Secretaries—A. D. Hall, M.A.; C. A. Kohn, Ph.D. (Recorder); T. K. Rose, D.Sc.; Dr. W. P. Wynne, F.R.S.

Committee—A. H. Allen; Sir William Roberts-Austen, K.C.B.; Sir William Crookes, F.R.S.; Prof. H. B. Dixon, F.R.S.; Ludwig Mond, F.R.S.; J. H. Gladstone, F.R.S.; W. H. Pendlebury; Prof. J. Emerson Reynolds, F.R.S.; Sir Henry E. Roscoe, F.R.S.; T. E. Thorpe, F.R.S.; W. A. Tilden, F.R.S.

The Papers brought before the Section were as follows:—

President's Address—The Assimilation of Carbon by the Higher Plants.

Prof. Dewar—The Solidification of Hydrogen.

Report of the Committee on Preparing a New Series of Wave-length Tables of the Spectra of the Elements.

Report of the Committee on the Continuation of the Bibliography of Spectroscopy.

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VOL. LXXX., No. 2079.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

DOVER, 1899.

By HORACE T. BROWN, LL.D., F.R.S.,
President of the Section.

(Concluded from p. 142).

IF instead of taking the air from a height of three or four feet from the ground, we examine the stratum only one or two centimetres above the surface of a soil free from vegetation, we find, as might be expected, a very large increase in the amount of carbon dioxide, which may exceed, under these circumstances, 12 or 13 parts per 10,000 of air. Such a soil, in fact, gives off by diffusion into the surrounding air an amount of carbon dioxide which is comparable to that evolved by a respiring leaf; that is to say, about 50 c.c. per square metre per hour. This is probably a factor which has to be taken into account in considering the assimilative power of vegetation of very low growing habit, but in all other cases we may assume with safety that aerial plants have to take in their carbon dioxide from air in which its tension does not exceed $\frac{1}{10000}$ of an atmosphere.

The actual intake of carbon dioxide is determined by enclosing the entire leaf in specially constructed air-tight glazed cases, through which a sufficiently rapid air stream is passed. These cases are so arranged that the leaf can be enclosed whilst still attached to a plant which is growing out in the open under perfectly natural conditions, and some of them are sufficiently large to take the entire leaf of a sunflower.

The carbon dioxide content of the air is determined both before and after its passage through the apparatus; and since the amount of air passed is known, we have all the data requisite for determining the actual amount retained by the leaf.

An experiment generally lasts from five to six hours, and the carbon dioxide fixed in this time may amount to 150 c.c. or more, the actual error of determination being very small indeed.

For purposes of comparison the volumes are reduced to the actual number of cubic centimetres of the gas absorbed by a square metre of leaf in one hour, which of course necessitates an exact determination of the area of the leaf. This is most conveniently effected by printing the leaf on sensitised paper, and tracing round its outline with a planimeter set to read off square centimetres; a far more accurate and expeditious plan than that of cutting out a fac-simile of the leaf from paper of a known weight per unit of area.

If it is desired to estimate the assimilative power of a leaf in an atmosphere artificially enriched with carbon dioxide, the air stream before entering the leaf case is passed through a small tower containing fragments of marble, over which there drops a very slow stream of dilute acid, whose rate of flow is so proportioned to the air stream as to give about the desired enrichment with carbon dioxide. The stream of air is then divided, one part going on directly to the leaf case, whilst the other passes through a separate absorption apparatus and meter for the accurate determination of its carbon dioxide content.

In order to show the kind of results obtained in this manner I will give one or two examples.

A leaf of the sunflower, having an area of 617.5 sq. c.m., was enclosed in its case whilst still attached to the plant,

and was exposed to the strong diffuse light of a clouded sky for five and a half hours, air being passed over it at the rate of nearly 150 litres per hour. The content of the air in carbon dioxide as it entered the apparatus was 2.80 parts per 10,000, and this was reduced to 1.74 parts per 10,000 during its passage over the leaf. This corresponds to a total absorption of 139.95 c.c. of carbon dioxide, or to an intake of 412 c.c. per square metre per hour. If we assume that the average composition of the carbohydrates formed is that of a $C_6H_{12}O_6$ sugar, the above amount of carbon dioxide corresponds to the formation of 0.55 gm. of carbohydrate per square metre per hour. But we must bear in mind that the average tension of the carbon dioxide in the leaf case was only equal to 1.93 parts per 10,000—that is, only about seven-tenths of its tension in the normal air. A correction has therefore to be made if we wish to know how much the leaf would have taken in, under similar conditions of insolation, if it had been bathed with a current of air of sufficient rapidity to practically keep the amount of carbon dioxide constant at its normal amount of 2.8 per 10,000. We shall see later on that, well within the limits of this experiment, the intake is proportional to the tension, so that, applying this correction we may conclude that under identical conditions of insolation and temperature this leaf would have taken in an amount of carbon dioxide from the free air at a rate sufficient to produce 0.8 gm. of carbohydrate per square metre per hour. This is almost exactly equal to the assimilation rate of the sunflower which I deduced in 1892 from the indirect process of weighing equal areas of the leaf lamina before and after insolation, and it also agrees fairly well with some of Sachs's original experiments of a similar nature.

In another experiment made with the leaf of *Catalpa bignonioides* in full sunlight the amount of carbon dioxide in the air passing over the leaf fell from 2.80 to 1.79 parts per 10,000, the total hourly intake for the square metre being 344.8 c.c. When this is corrected for tension it corresponds to an assimilation in free air of 0.55 gm. of carbohydrate per square metre per hour.

An increase in the intensity of the daylight, as might be expected, influences to some extent the rate of intake of atmospheric carbon dioxide; but providing the illumination has reached a certain minimum amount, a further increase in the radiant energy incident on the leaf does not result in anything like a proportional amount of assimilation. We have found, for instance, that the rate of assimilation of a sunflower leaf, exposed to the clear northern sky on a warm summer's day, was about one-half of what it was when the leaf was turned round so as to receive the direct rays of the sun almost normal to its surface. Now in this latter case the actual radiant energy received by the leaf was at least twelve times greater than was received from the northern sky, but the assimilation was only doubled.

These differences in the effect of great variation of illumination become still less marked when we use air which has been artificially enriched with carbon dioxide. In one instance of this kind, for example, we found the assimilation in the full diffuse light of the northern sky to be 87 per cent of what it was in direct sunshine.

This brings me to another interesting point on which I have already touched slightly—the enormous influence which slight changes in the carbon dioxide content of the air exert on the rate of its ingress into the assimilating leaf.

With a constant illumination, either in direct sunlight or diffuse light, the assimilatory process responds to the least variation in the carbon dioxide, and within certain limits, not yet clearly defined, the intake of that gas into the leaf follows the same rule as the one which holds good with regard to the absorption of carbon dioxide by a freely exposed surface of a solution of caustic alkali; that is to say, from air containing small but variable quantities of carbon dioxide the intake is directly proportional to the tension of that gas.

A single experiment will be sufficient to illustrate this.

A large sunflower leaf, still attached to the plant, and exposed to a clear northern sky, gave an assimilation rate equal to 0.331 grm. of carbohydrate per square metre per hour, when air was passed containing an average amount of 2.22 parts of carbon dioxide per 10,000. When the experiment was repeated under similar conditions of illumination, but with air containing 14.82 parts of CO_2 per 10,000, the intake corresponded to an hourly formation of 2.409 grms. of carbohydrate per square metre. The ratio of the tensions of the carbon dioxide in the two experiments is 1 to 6.7 and the assimilatory ratio is 1 to 7.2, so that the increased assimilation is practically proportional to the increase in tension of the carbon dioxide.

Since an increase of carbon dioxide in the atmosphere surrounding a leaf is followed by increased assimilation even in diffuse daylight, it is clear that, under all ordinary conditions of illumination, the rays of the right degree of refrangibility for producing decomposition of carbon dioxide are largely in excess of the power of the leaf to utilise them. Under natural conditions this excess of radiant energy of the right wave-length must, from the point of view of the assimilatory process, be wasted, owing to the limitation imposed by the high degree of dilution of atmospheric carbon dioxide. But although the actual manufacture of new material within the leaf lamina is so largely influenced by small variations in the carbon dioxide of the air, we are not justified in concluding that the plant *as a whole* will necessarily respond to such changes in atmospheric environment, since the complex physiological changes involved in metabolism and growth may have become so intimately correlated that the perfect working of the mechanism of the entire plant may now only be possible in an atmosphere containing about three parts of carbon dioxide in 10,000.

We have commenced a series of experiments which will, I hope, throw considerable light on this point, but the work is not at present in a sufficiently advanced state for me to make more than a passing allusion to it.

The penetration of the highly diluted carbon dioxide of the atmosphere into the interior air spaces of the leaf on its way to the active centres of assimilation must, in the first instance, be a purely physical process, and no explanation of this can be accepted which does not conform to the physical properties of the gases involved.

Since there is no mechanism in the leaf capable of producing an ebb and flow of gases within the air spaces of the mesophyll in any way comparable with the movements of the tidal air in the lungs of animals; and since, also, the arrangement of the stomatic openings is such as to effect a rapid equalisation of pressure within and without the leaf, we must search for the cause of the gaseous exchange, not in any mass movement, but in some form of diffusion. This may take place in the form of *open diffusion* through the minute stomatic apertures, which are in communication both with the outer air and the intercellular spaces, or the gaseous exchange may take place through the cuticle and epidermis by a process of *gaseous osmosis*, similar to that which Graham investigated in connection with certain colloid septa.

For many years there has been much controversy as to which form of gaseous diffusion is the more active in producing the natural interchanges of gases in the leaf. The present occasion is not one in which full justice can be done to the large amount of experimental work which has from time to time been carried out in this direction. Up to comparatively recently the theory of cuticular osmosis has been the one which has been more commonly accepted, free diffusion through the open stomata being considered quite subsidiary. In 1895, however, Mr. F. F. Blackman brought forward two remarkable papers which opened up an entirely new aspect of the subject. After showing the fallacy underlying certain experiments of Boussingault, which had been generally supposed to prove the osmotic

theory of exchange, Mr. Blackman gave the results of his own experiments with a new and beautifully constructed apparatus, which enabled him to measure very minute quantities of carbon dioxide given off from small areas of the upper and under sides of a respiring leaf, and also to determine the relative intake of carbon dioxide by the two surfaces during assimilation in air artificially charged with that gas. The conclusions drawn are that respiratory egress, and assimilatory ingress of carbon dioxide do not occur in the upper side of a leaf if this is devoid of stomatic openings, and that when these openings exist on both the upper and under sides the gaseous exchanges of both physiological processes are directly proportional to the number of stomata on equal areas; hence in all probability the exchanges take place only through the stomata.*

These observations of Mr. Blackman are of such far-reaching importance, and lead, as we shall see presently, to such remarkable conclusions with regard to the rate of diffusion of atmospheric carbon dioxide, that we felt constrained to inquire into the matter further, and for this purpose we employed a modified form of the apparatus which we have used throughout our work on assimilation. This was so arranged that a current of ordinary air could be passed, just as in Mr. Blackman's experiments, over the upper and lower surface of a leaf separately, the increase or decrease in the carbon dioxide content of the air being determined by absorption and titration in the manner I have already alluded to.

In this way we were able to employ comparatively large leaf areas, and to continue an experiment for several hours, so that we had relatively large amounts of carbon dioxide to deal with, and the ratios of gaseous exchange of the two sides of the leaf could consequently be determined with considerable accuracy.

Our results, on the whole, are decidedly confirmatory of Mr. Blackman's observations. The side of a leaf which is devoid of stomatic openings certainly neither allows any carbon dioxide to escape during respiration, nor does it permit the ingress of that gas when the conditions are favourable for assimilation. On the other hand, when stomata exist on both the upper and under sides of a leaf, gaseous exchanges take place through both surfaces, and, as a rule, in some sort of rough proportion to the distribution of the openings. There is, however, under strong illumination, a greater intake of carbon dioxide through the upper surface than would be expected from a mere consideration of the ratio of distribution of the stomata.† Nevertheless, the general connection between gaseous exchange and distribution of stomata is so well brought

* There is one important fact to be borne in mind when considering how far these observations exclude the possibility of cuticular osmosis. In the many leaves we have examined, Mr. Escombe and I have found that the occurrence of stomata on the upper surface of the leaf is always correlated with a much less dense palisade parenchyma. The cuticle and epidermis under these conditions are in a much more favourable state to allow carbon dioxide to pass into the leaf by osmosis than when the closely packed palisade cells abut against the epidermis, as they do when this is imperforate.

† Granted that the stomata constitute the paths of gaseous exchange, it is clear that the amount of diffusion through them, other things being equal, must depend very largely on the extent to which they are opened. The delicate self-regulating apparatus which governs the size of the openings is so readily influenced, amongst other things, by difference of illumination, that *à priori* we should not expect the stomata on the upper surface of an insolated leaf to be in the same condition as those of the more shaded lower surface. This may very well account for the stomatic ratio of the two sides not being in closer correspondence with the assimilatory ratios, as found in most of our experiments carried out in bright sunlight. In light of lesser intensity there is always a closer correspondence of the two ratios.

There is also another possible explanation of the fact. Since we have good reason to believe that the principal part of the assimilatory work is carried on by the palisade parenchyma, which occurs in the upper side of the leaf, the tension of the carbon dioxide in the air spaces of that part of the mesophyll is probably less than it is in the spongy parenchyma. There will, therefore, be a higher "diffusion gradient" between the carbon dioxide of the outer and inner air in the former case than in the latter, and this would certainly tend to a more rapid diffusion through the openings in the upper side of the leaf.

out that we must regard it as highly probable that these minute openings are the true paths by which the carbon dioxide enters and leaves the leaf.

We must now look at certain physical consequences which proceed from this assumption, and see how far they can be justified by the known or ascertainable properties of carbon dioxide at very low tensions.

The leaf of *Catalpa bignonioides* is hypostomatic, and therefore takes in carbon dioxide only by its lower sur-

posed surface of a solution of caustic alkali. But if the intake of the gas is confined to the stomatic openings of the leaf, its velocity of ingress must be very much greater than this.

We have carefully determined the number of stomata occurring on a given area of this particular leaf, and also the dimensions of the openings, and find that the total area of the openings, supposing them to be dilated to the fullest possible extent, amounts to just under *one per cent*

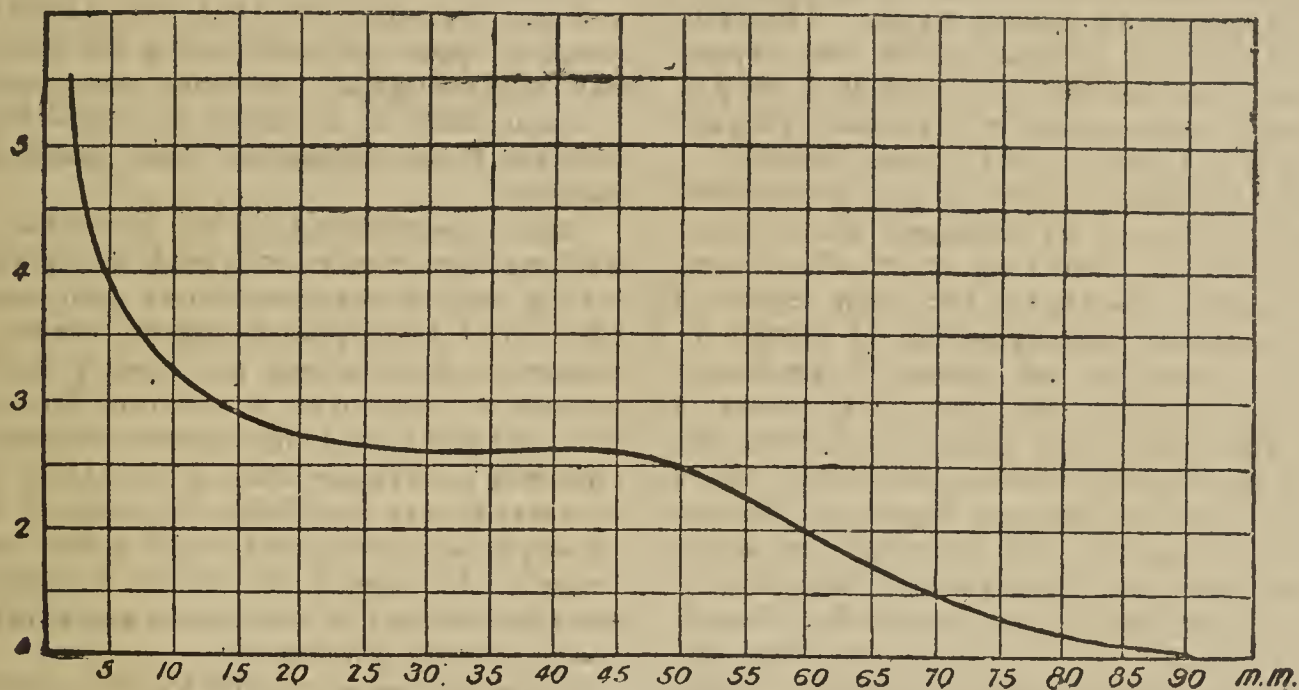


FIG. 1.

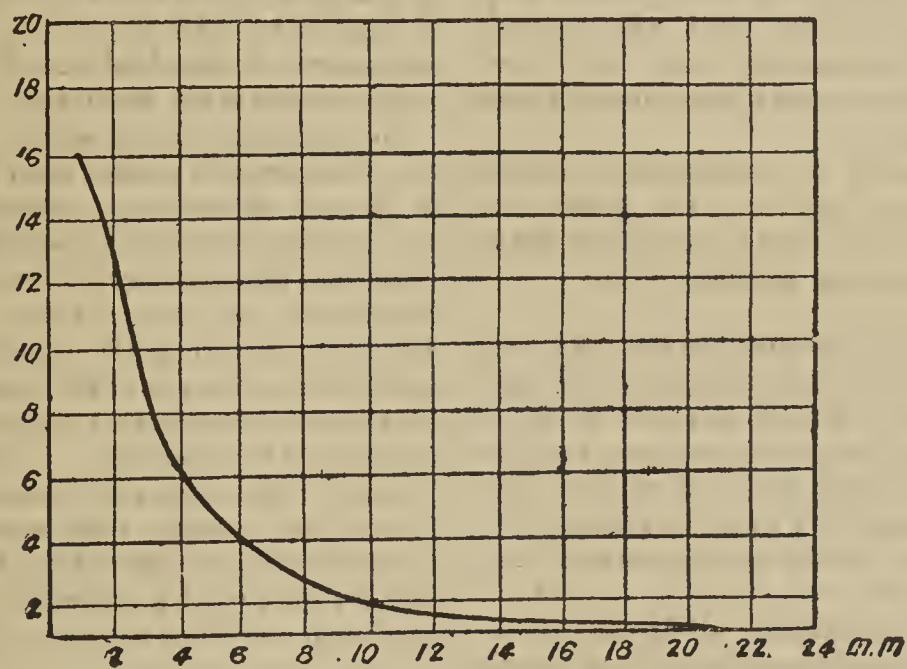


FIG. 2.

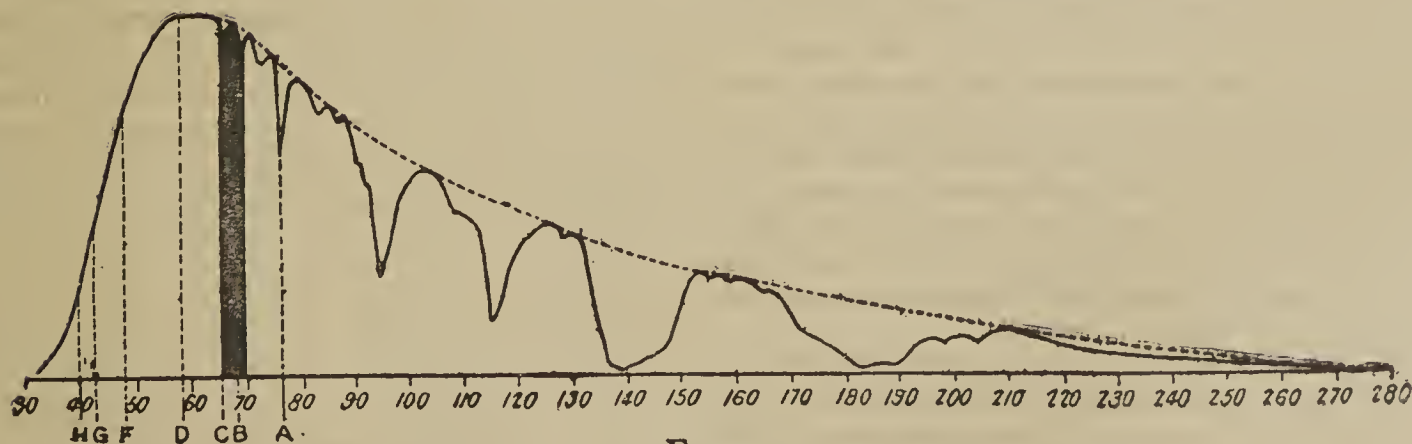


FIG. 3.

face. Under favourable conditions it is quite possible, during assimilation, to obtain an intake of atmospheric carbon dioxide into this leaf at the rate of 700 c.c. per square metre per hour (measured at 0° and 760 m.m.), corresponding to an average linear velocity of the carbon dioxide molecules of 3.8 centimetres per minute, supposing the intake to be distributed evenly over the whole of the lower leaf surface. This velocity is almost exactly one-half of that at which carbon dioxide will enter a freely ex-

posed surface of a solution of caustic alkali. It follows from this that the average velocity of the atmospheric carbon dioxide in passing through these openings must be 380 centimetres per minute—that is to say, just *fifty* times greater than into a freely exposed absorbent surface of alkali. In other words, supposing every one of the stomatic openings of this leaf could be filled up with a solution of caustic alkali, the absorbent power of the leaf as a whole would only be $\frac{1}{50}$ of what it actually is when assimilating.

These are some of the consequences which flow from an acceptance of the hypothesis of stomatic exchange, and it appeared to be impossible to accept that hypothesis unreservedly without some collateral evidence that these comparatively high velocities of diffusion are physically possible when dealing with such low gradients of tension as must necessarily exist when the highest amount of carbon dioxide does not exceed 0.03 per cent.

The well-known general law expressing the rate of the spontaneous intermixture of two gases when there is no intervening septum, was, as everyone knows, established by Graham, and the more elaborate investigations of Loschmidt many years later served to confirm the general accuracy of this law, and to show that, within very narrow limits, the diffusion constant varies in different gases inversely as the square roots of their densities.

But a mere knowledge of the diffusion constants of air and carbon dioxide does not, as far as I can see, materially assist us in the particular case we have under consideration. In order to gain some idea of what is actually possible in the way of stomatic diffusion in an assimilating leaf we must know something of the *actual rate* at which atmospheric carbon dioxide can be made to pass into a small chamber containing air at the outside tension, but in which the carbon dioxide is kept down almost to the vanishing point by some rapid process of absorption; and we must also determine the influence of varying the size of the aperture through which the diffusion takes place.

Our attempts to answer these questions experimentally have led us into a long investigation, which promises to be of wider interest than we had first imagined. I only propose to give on this occasion a general account of the results so far as they affect the physical question of the intake of carbon dioxide into the plant.

When a shallow vessel containing a solution of caustic alkali is completely covered, the air above the liquid is very speedily deprived of the whole of its carbon dioxide. If we now imagine a hole to be made in the cover of the vessel, carbon dioxide will enter the air space by free diffusion, and its amount can be very accurately determined by subsequent titration in the manner I have previously referred to. The time occupied by the experiment and the dimensions of the aperture being known, we can express the results in actual amounts of carbon dioxide passing through unit area of aperture in unit of time; or, since the tension of that gas in the outer air is known, we can express the average rate of the carbon dioxide molecules across the aperture in terms of actual measurement, say centimetres per minute.

We have made a very large number of experiments of this kind, using, in the first instance, dishes of about 9 c.m. in diameter, and varying the size of the holes in the cover, the air space over the absorbent liquid being always the same.

The accompanying curve, Fig. 1, illustrates the effect which a gradually decreasing orifice has on the rate of diffusion of atmospheric carbon dioxide under these conditions. The diameters of the orifice in millimetres are given on the abscissa line, and the rates of diffusion through equal areas of the apertures are taken as ordinates, the rate of absorption in the open dish under similar conditions being taken as unity.

It will be seen that in the first instance a gradual reduction of the diameter of the opening is accompanied by a very regular increase in the rate of passage of the carbon dioxide until a diameter of about 50 m.m. is reached; that is to say, up to a point at which about two-thirds of the area of the dish is covered. A further progressive diminution in the size of the aperture makes comparatively little difference in the diffusion rate until we reach about 20 m.m., beyond which the curve again begins to rise, increasing rapidly in steepness as the apertures become smaller.

The experiments with open dishes are too crude for a study of the influence of very small apertures, so for this part of our work we constructed a special form of apparatus

which has enabled us to determine the relative rates of diffusion through orifices in thin metal plates ranging down to 1 m.m. in diameter.

I have plotted the results of such a series of experiments (see Fig. 2), showing the relative rates of diffusion of atmospheric carbon dioxide through equal areas of apertures between 20 m.m. and 1 m.m. in diameter, under constant conditions, and it will be noticed how very steep the curve becomes after diameters of 5 or 6 m.m. are reached.

The speed at which the diffusion of atmospheric carbon dioxide takes place through unit area of an orifice of 1 m.m. in diameter is just sixteen times as fast as it is through unit area of an aperture of 20 m.m.; and since we know that the rate of passage in the latter case is two and a half times greater than the absorption rate of an equal area of a freely exposed surface of a solution of caustic alkali, we arrive at the conclusion that, under the particular conditions of our experiment, the diffusion rate through an aperture of 1 m.m. is *forty times* greater than the rate of absorption of a free alkaline surface of equal area.

This corresponds to an actual average rate of passage of the molecules of the atmospheric carbon dioxide of about 266 centimetres per minute.

Now, we have already seen, in the case of a Catalpa leaf, that if the gaseous exchange during assimilation goes on only through the stomatic openings, we require a minimum velocity of something like 380 centimetres per minute—a velocity which we are sensibly approaching in our experiments with apertures of about 1 m.m. in diameter. But the effective area of a stomatic opening of the Catalpa leaf is equal to that of a circle with a diameter of less than $\frac{1}{100}$ m.m., and since our experiments indicate a very rapid increase in the velocity of diffusion as the aperture is diminished, it is clear that no difficulty, as regards the physics of the question, can be raised against the idea that atmospheric carbon dioxide reaches the active centres of assimilation by a process of free diffusion through the leaf stomata.

One of the most interesting problems connected with plant assimilation relates to the efficiency of a green leaf as an absorber and transformer of the radiant energy incident upon it.

It is already well known that the actual amount of energy stored up in the products of assimilation bears a very small proportion to the total amount reaching the leaf: in other words, the leaf, regarded from a thermodynamic point of view, is a machine with a very low "economic coefficient." We require, however, to know much more than this, and to ascertain, amongst other things, how the efficiency of the machine varies under different conditions of insolation, and in atmospheres containing varying amounts of carbon dioxide.

The measure of the two principal forms of work done within the leaf, the vaporisation of the transpiration water on the one hand, and the reduction of carbon dioxide and water to the form of carbohydrates on the other, can be ascertained by modifying our experiments in such a manner as to allow the transpiration water to be determined, as well as the intake of carbon dioxide.

For the actual measurement of the total energy incident on the leaf under various conditions we are now using one of Professor Callendar's recording radiometers of specially delicate construction, which will be ultimately calibrated in calories. This instrument gives promise of excellent results, but up to the present time the work we have done with it is not sufficiently advanced for me to describe. We may, however, obtain a very fair idea of the variation in the efficiency of a leaf from one or two examples in which the amount of incident energy was deduced from other considerations.

In the case of a sunflower leaf exposed to the strong sunlight of a brilliant day in August the average amount of radiant energy falling on the leaf during the five hours

occupied by the experiment was estimated at 600,000 calories per square metre per hour. The average hourly transpiration of water during that time was at the rate of 275 c.c. per square metre, and the assimilated carbohydrate, estimated by the intake of carbon dioxide, was at the rate of 0.8 gm. per square metre per hour.

The vaporisation of 275 c.c. of water must have required the expenditure of 166,800 calories, and the endothermic production of 0.8 gm. of carbohydrate (taking the heat of combustion at 4000 gm. calories) corresponds to the absorption of 3200 calories. Thus, as the final result under these particular conditions of experiment, we find that the leaf has absorbed and converted into internal work about 28 per cent of the total radiant energy incident on it, 27.5 per cent being used up in the vaporisation of water, and only *one-half per cent* in the actual work of assimilation.

In strong diffuse light, such as that from a northern sky on a clear summer's day, the leaf has a higher "economic coefficient," using that term in relation to the permanent storage of energy in the assimilatory products. In one instance of this kind in which the total energy received by the leaf was approximately 60,000 calories per square metre per hour, it was found that 96 c.c. of water were evaporated and 0.41 gm. of carbohydrate was formed for the same area and time. This indicates an absorption and utilisation by the leaf of something like 95 per cent of the incident energy, of which 2.7 per cent has been made use of for actual work of assimilation as against 0.5 per cent in brilliant sunshine.*

From what I have said previously about the effect of increased tension of carbon dioxide on the rate of assimilation, it must follow that the "efficiency" of a leaf as regards the permanent storage of energy must, *cæteris paribus*, be increased when small additions of that gas are made to the surrounding air.

In one such instance, in which the air had been enriched with carbon dioxide to the extent of about five-and-a-half times the normal amount, it was estimated that the "efficiency" of the leaf for bright sunshine was raised from 0.5 to 2.0 per cent.

Up to the present we have been regarding the efficiency of the assimilatory mechanism of a plant in reference to the *total* energy of all grades which falls upon the leaf. It is of course well known that the power of decomposing carbon dioxide is limited to rays of a certain refrangibility, and the researches of Timiriazeff, Engelmann, and others leaves little room to doubt that the rays of the spectrum which are instrumental in producing the reaction in the chloroplastids have a distinct relation to the absorption-bands of the leaf-chlorophyll. By far the greater amount of the assimilatory work, probably more than 90 per cent of it, is effected by the rays which correspond to the principal absorption-band in the red, lying between wavelengths 6500 and 6975.† If, therefore, we express the distribution of energy in a normal solar spectrum in the

form of a curve, we have the means of approximately determining the *maximum theoretical efficiency* of a green leaf; that is to say, the maximum amount of assimilatory work which could be produced, supposing the conditions so favourable as to admit of the whole of the energy corresponding to this absorption-band being stored up within the leaf.

It is not without interest to get an approximate idea of this theoretical maximum.

For this purpose I have here reproduced a curve given by Professor S. P. Langley, representing the distribution of energy at the sea-level in the normal spectrum of a vertical sun shining in a clear sky (Fig. 3). The total amount of incident energy represented by the whole area of the curve is 1.7 calories per square centimetre per minute, or 1,020,000 calories per square metre per hour.

I have drawn a thick black vertical band in the red end of the spectrum corresponding in position and breadth with the principal absorption band of chlorophyll as seen in a green leaf. By integration it may be shown that the area of this part of the curve is about 6.5 per cent of that of the whole curve, so that this value represents something like the theoretical maximum efficiency of a leaf in bright vertical sunshine, supposing the conditions could be made so favourable as to result in a complete filtering-out and utilisation of the whole of the rays of the right period for producing decomposition of carbon dioxide.

This maximum efficiency expressed in calories per square metre per hour is 66,300, corresponding to the heat of formation of about 16.5 grms. of carbohydrate. Under the most favourable conditions we have employed up to the present we have not obtained a larger production than about 3.0 grms. of carbohydrate per square metre per hour, or about 18 per cent of the theoretical maximum; but this was in air containing only 16.4 parts of carbon dioxide per 10,000, which must be very far below the true optimum amount.

The brilliant discoveries of recent years on the constitution and synthesis of the carbohydrates have not brought us sensibly nearer to an explanation of the first processes of the reduction of carbon dioxide in the living plant. The hypothesis of Baeyer still occupies the position it did when it was first put forward nearly thirty years ago, although it has, it is true, received a certain amount of support from the observations of Bokorny, who found that formaldehyde can, under certain conditions, contribute to the building up of carbohydrates in the chloroplasts.

The changes which go on in the living cell are so rapid, and are of such a complex kind, that there seems little or no hope of ascertaining the nature of the first steps in the process unless we can artificially induce them under much simpler conditions.

The analogy which exists between the action of chlorophyll in the living plant and that of a *chromatic sensitiser* in a photographic plate, was, I believe, first pointed out by Captain Abney, and was more fully elaborated by Timiriazeff, who was inclined to regard chlorophyll as the sensitiser *par excellence*, since it absorbs and utilises for the assimilatory process the radiations corresponding approximately to the point of maximum energy in the normal spectrum. The view which Timiriazeff has put forward, that there is a mere physical transference of vibrations of the right period from the absorbing chlorophyll to the reacting carbon dioxide and water, is, I think, far too simple an explanation of the facts. Chromatic sensitisers have been shown to act by reason of their antecedent decomposition and not by direct transference of energy, and the same probably holds good with regard to chlorophyll, which is also decomposed by the rays which it absorbs. We must probably seek for the first and simplest stages of the assimilatory process in the interaction of the reduced constituents of the chlorophyll and the elements of carbon dioxide and water, the combinations so formed being again split up in another direction by access of energy from without.

* The principal factor which determines the amount of transpiration in a plant must be the amount of radiation falling on it. It is essential that the water-bearing mechanism should be able to keep up a good supply of water to the leaf lamina in order to prevent the temperature rising to a dangerously high point. This "safety valve" function of the transpiration current is not always sufficiently borne in mind, and we are too apt to think that the plant requires these enormous amounts of water in order to supply itself with the requisite mineral salts. The absolute necessity for the supply as a dissipator of energy will become evident by taking one or two facts into consideration. A square metre of the lamina of the leaf of a sunflower weighs about 250 grms., and its specific heat is about 0.9. We have seen that the hourly transpiration in bright sunshine may be as much as 275 c.c. per square metre, requiring the expenditure of 162,800 calories, and it therefore follows that, if the loss of water were stopped, the temperature of the leaf would rise at the rate of more than 12° C. *per minute*. In making our experiments in glazed cases it has sometimes been very interesting to watch the result of any accidental stoppage of the water-current in the leaf-stalk, and the almost instantaneous effect this has in destroying the leaf when the insolation is of high intensity.

† These limits are those of the band as measured by passing sunlight through the leaf itself. In an alcoholic solution of chlorophyll the band lies between λ 6400 and λ 6850. I must here express my thanks to Mr. Charles A. Schunck for having kindly undertaken to make these measurements for me.

The failure of all attempts to produce such a reaction under artificial conditions is, I think, to be accounted for by the neglect of one very important factor. We are dealing with a reaction of a highly endothermic nature, which is probably also highly *reversible*, and on this account we cannot expect any sensible accumulation of the products of change unless we employ some means for removing them from the sphere of action as fast as they are formed.

In the plant this removal is provided for by the living elements of the cell, by the chloroplast, assisted no doubt by the whole of the cytoplasm. We have here, in fact, the analogue of the *chemical sensitisers* of a photographic plate, which act as halogen absorbers and so permit a sensible accumulation of effect on the silver salts.

When we have succeeded in finding some simple chemical means of fixing the initial products of the reduction of carbon dioxide, then, and then only, may we hopefully look forward to reproducing in the laboratory the first stages of the great synthetic process of Nature on which the continuance of all life depends.

ADDRESS TO THE
MATHEMATICAL AND PHYSICAL SECTION
OF THE
BRITISH ASSOCIATION.
DOVER, 1899.

By J. H. POYNTING, D.Sc., F.R.S.,
President of the Section.

THE members of this Section will, I am sure, desire me to give expression to the gratification that we all feel in the realisation of the scheme first proposed from this chair by Dr. Lodge, the scheme for the establishment of a National Physical Laboratory. It would be useless here to attempt to point out the importance of the step taken in the definite foundation of the Laboratory, for we all recognise that it was absolutely necessary for the due progress of physical research in this country. It is matter for congratulation that the initial guidance of the work of the Laboratory has been placed in such able hands.

While the investigation of Nature is ever increasing our knowledge, and while each new discovery is a positive addition never again to be lost, the range of the investigation and the nature of the knowledge gained form the theme of endless discussion. And in this discussion, so different are the views of different schools of thought, that it might appear hopeless to look for general agreement, or to attempt to mark progress.

Nevertheless, I believe that in some directions there has been real progress, and that physicists, at least, are tending towards a general agreement as to the nature of the laws in which they embody their discoveries, of the explanations which they seek to give, and of the hypotheses they make in their search for explanations.

I propose to ask you to consider the terms of this agreement, and the form in which, as it appears to me, they should be drawn up.

The range of the physicist's study consists in the visible motions and other sensible changes of matter. The experiences with which he deals are the impressions on his senses, and his aim is to describe in the shortest possible way how his various senses have been, will be, or would be affected.

His method consists in finding out all likenesses, in classing together all similar events, and so giving an account as concise as possible of the motions and changes observed. His success in the search for likenesses and his striving after conciseness of description lead him to imagine such a constitution of things that likenesses exist even where they elude his observation, and he is thus enabled to simplify his classification on the assumption that the constitution thus imagined is a reality. He is

enabled to predict on the assumption that the likenesses of the future will be the likenesses of the past.

His account of Nature, then, is—as it is often termed—a descriptive account.

Were there no similarities in events, our account of them could not rise above a mere directory, with each individual event entered up separately with its address. But the similarities observed enable us to class large numbers of events together, to give general descriptions, and indeed to make, instead of a directory, a readable book of science, with laws as the headings of the chapters.

These laws are, I believe, in all cases brief descriptions of observed similarities. By way of illustration let us take two or three examples.

The law of gravitation states that to each portion of matter we can assign a constant—its mass—such that there is an acceleration towards it of other matter proportional to that mass divided by the square of its distance away. Or all bodies resemble each other in having this acceleration towards each other.

Hooke's law for the case of a stretched wire states that each successive equal small load produces an equal stretch, or states that the behaviour of the wire is similar for all equal small pulls.

Joule's law for the heat appearing when a current flows in a wire states that the rate of heat development is proportional to the square of the current multiplied by the resistance, or states that all the different cases resemble each other in having $H \div C^2 R t$ constant.

And, generally, when a law is expressed by an equation, that equation is a statement that two different sets of measurements are made, represented by the terms on the two sides of the equation, and that all the different cases resemble each other in that the two sets have the constant relation expressed by the equation. Accurate prediction is based on the assumption that when we have made the measurements on the one side of the equation we can tell the result of the measurements implied on the other side.

If this is a true account of the nature of physical laws, they have, we must confess, greatly fallen off in dignity. No long time ago they were quite commonly described as the Fixed Laws of Nature, and were supposed sufficient in themselves to govern the universe. Now we can only assign to them the humble rank of mere descriptions, often tentative, often erroneous, of similarities which we believe we have observed.

The old conception of laws as self-sufficing governors of Nature was, no doubt, a survival of a much older conception of the scope of physical science, a mode of regarding physical phenomena which had itself passed away.

I imagine that originally man looked on himself and the result of his action in the motions and changes which he produced in matter, as the one type in terms of which he should seek to describe all motions and changes. Knowing that his purpose and will were followed by motions and changes in the matter about him, he thought of similar purpose and will behind all the motions and changes which he observed, however they occurred; and he believed, too, that it was necessary to think thus in giving any consistent account of his observations. Taking this anthropomorphic—or, shall we say, psychical—view, the laws he formulated were not merely descriptions of similarities of behaviour, but they were also expressions of fixed purpose and the resulting constancy of action. They were commands given to matter which it must obey.

The psychical method, the introduction of purpose and will, is still appropriate when we are concerned with living beings. Indeed it is the only method which we attempt to follow when we are describing the motions of our fellow-creatures. No one seeks to describe the motions and actions of himself and of his fellow-men, and to classify them without any reference to the similarity of purpose when the actions are similar. But as the study

of Nature progressed, it was found to be quite futile to bring in the ideas of purpose and will when merely describing and classifying the motions and changes of non-living matter. Purpose and will could be entirely left out of sight, and yet the observed motions and changes could be described, and predictions could be made as to future motions and changes. Limiting the aim of physical science to such description and prediction, it gradually became clear that the method was adequate for the purpose, and over the range of non-living matter, at least, the psychical yielded to the physical. Laws ceased to be commands analogous to legal enactments, and became mere descriptions. But during the passage from one position to the other, by a confusion of thought which may appear strange to us now that we have finished the journey, though no doubt it was inevitable, the purpose and will of which the laws had been the expression were put into the laws themselves; they were personified and made to will and act.

Even now these early stages in the history of thought can be traced by survivals in our language, survivals due to the ascription of moral qualities to matter. Thus gases are still sometimes said to obey or to disobey Boyle's Law as if it were an enactment for their guidance, and as if it set forth an ideal, the perfect gas, for their imitation. We still hear language which seems to imply that real gases are wanting in perfection, in that they fail to observe the exact letter of the law. I suppose on this view we should have to say that hydrogen is nearest to perfection; but then we should have to regard it as righteous over-much, a sort of Pharisee among gases which overshoots the mark in its endeavour to obey the law. Oxygen and nitrogen we may regard as good enough in the affairs of everyday life. But carbon dioxide and chlorine and the like are poor sinners which yield to temptation and liquefy whenever circumstances press at all hardly on them.

There is a similar ascription of moral qualities when we judge bodies according to their fulfilment of the purpose for which we use them, when we describe them as good or bad radiators, good or bad insulators, as if it were a duty on their part to radiate well, or insulate well, and as if there were failures on the part of Nature to come up to the proper standard.

These are of course mere trivialities, but the reaction of language on thought is so subtle and far-reaching that, risking the accusation of pedantry, I would urge the abolition of all such picturesque terms. In our quantitative estimates let us be content with "high" or "low," "great" or "small," and let us remember that there is no such thing as a failure to obey a physical law. A broken law is merely a false description.

Concurrently with the change in our conception of physical law has come a change in our conception of physical explanation. We have not to go very far back to find such a statement as this, that we have explained anything when we know the cause of it, or when we have found out the reason why—a statement which is only appropriate on the psychical view. Without entering into any discussion of the meaning of cause, we can at least assert that that meaning will only have true content when it is concerned with purpose and will. On the purely physical or descriptive view, the idea of cause is quite out of place. In description we are solely concerned with the "how" of things, and their "why" we purposely leave out of account. We explain an event not when we know "why" it happened, but when we show "how" it is like something else happening elsewhere or otherwhen—when, in fact, we can include it as a case described by some law already set forth. In explanation, we do not account *for* the event, but we improve our account *of* it by likening it to what we already knew.

For instance, Newton explained the falling of a stone when he showed that its acceleration towards the earth was similar to and could be expressed by the same law as the acceleration of the moon towards the earth.

He explained the air disturbance we call "sound" when he showed that the motions and forces in the pressure waves were like motions and forces already studied.

Franklin explained lightning when and so far as he showed that it was similar in its behaviour to other electric discharges.

Here I do not fear any accusation of pedantry in joining those who urge that we should adapt our language to the modern view. It would be a very real gain, a great assistance to clear thinking, if we could entirely abolish the word "cause" in physical description, cease to say "why" things happen unless we wish to signify an antecedent purpose, and be content to own that our laws are but expressions of "how" they occur.

The aim of explanation, then, is to reduce the number of laws as far as possible, by showing that laws, at first separated, may be merged in one; to reduce the number of chapters in the book of science by showing that some are truly mere sub-sections of chapters already written.

To take an old but never worn-out metaphor, the physicist is examining the garment of Nature, learning of how many, or rather of how few, different kinds of thread it is woven, finding how each separate thread enters into the pattern, and seeking from the pattern woven in the past to know the pattern yet to come.

How many different kinds of thread does Nature use?

So far, we have recognised some eight or nine, the number of different forms of energy which we are still obliged to count as distinct. But this distinction we cannot believe to be real. The relations between the different forms of energy, and the fixed rate of exchange when one form gives place to another, encourage us to suppose that if we could only sharpen our senses, or change our point of view, we could effect a still further reduction. We stand in front of Nature's loom as we watch the weaving of the garment; while we follow a particular thread in the pattern it suddenly disappears, and a thread of another colour takes its place. Is this a new thread, or is it merely the old thread turned round and presenting a new face to us? We can do little more than guess. We cannot get to the other side of the pattern, and our minutest watching will not tell us all the working of the loom.

Leaving the metaphor, were we true physicists, and physicists alone, we should, I suppose, be content to describe merely what we observe in the changes of energy. We should say, for instance, that so much kinetic energy ceases, and that so much heat appears, or that so much light comes to a surface, and that so much chemical energy takes its place. But we have to take ourselves as we are, and reckon with the fact that though our material is physical, we ourselves are psychical. And, as a mere matter of fact, we are not content with such discontinuous descriptions. We dislike the discontinuity and we think of an underlying identity. We think of the heat as being that which a moment before was energy of visible motion, we think of the light as changing its form alone and becoming itself the chemical energy. Then to our passive dislike of discontinuity we join our active desire to form a mental picture of what may be going on, a picture like something which we already know. Coming on these discontinuities our ordinary method of explanation fails, for they are not obviously like those series of events in which we can trace every step. We then imagine a constitution of matter and modifications of it corresponding to the different kinds of energy, such that the discontinuities vanish, and such that we can picture one form of energy passing into another and yet keeping the same in kind throughout. We are no longer content to describe what we actually see or feel, but we describe what we imagine we should see or feel if our senses were on quite another scale of magnitude and sensibility. We cease to be physicists of the real and become physicists of the ideal.

To form such mental pictures we naturally choose the sense which makes such pictures most definite, the sense of sight, and think of a constitution of matter which

shall enable us to explain all the various changes in terms of visible motions and accelerations. We imagine a mechanical constitution of the universe.

We are encouraged in this attempt by the fact that the relations in this mechanical conception can be so exactly stated, that the equations of motion are so very definite. We have, too, examples of mechanical systems, of which we can give accounts far exceeding in accuracy the accounts of other physical systems. Compare, for instance, the accuracy with which we can describe and foretell the path of a planet with our ignorance of the movements of the atmosphere as dependent on the heat of the sun. The planet keeps to the astronomer's timetable, but the wind still bloweth almost where it listeth.

The only foundation which has yet been imagined for this mechanical explanation—if we may use "explanation" to denote the likening of our imaginings to that which we actually observe—is the atomic and molecular hypothesis of matter. This hypothesis arose so early in the history of science that we are almost tempted to suppose that it is a necessity of thought, and that it has a warrant of some higher order than any other hypothesis which could be imagined. But I suspect that if we could trace its early development we should find that it arose in an attempt to explain the phenomena of expansion and contraction, evaporation and solution. Were matter a continuum we should have to admit all these as simple facts, inexplicable in that they are like nothing else. But imagine matter to consist of a crowd of separate particles with interspaces. Contraction and expansion are then merely a drawing in and a widening out of the crowd. Solution is merely the mingling of two crowds, and evaporation merely a dispersal from the outskirts. The most evident properties of matter are then similar to what may be observed in any public meeting.

For ages the molecular hypothesis hardly went further than this. The first step onward was the ascription of vibratory motion to the atoms to explain heat. Then definite qualities were ascribed, definite mutual forces were called into play to explain elasticity and other properties or qualities of matter. But I imagine its first really great achievement was its success in explaining the law of combining proportions, and next to that we should put its success in explaining many of the properties of gases.

While light was regarded as corpuscular—in fact molecular, and while direct action at a distance presented no difficulty, the molecular hypothesis served as the one foundation for the mechanical representation of phenomena. But when it was shown that infinitely the best account of the phenomena of light could be given on the supposition that it consisted of waves, something was needed, as Lord Salisbury has said, to wave, both in the interstellar and in the intermolecular spaces. So the hypothesis of an ether was developed, a necessary complement of that form of the molecular hypothesis in which matter consists of discrete particles with matter-free intervening spaces.

Then Faraday's discovery of the influence of the dielectric medium in electric actions led to the general abandonment of the idea of action at a distance, and the ether was called in to aid matter in the explanation of electric and magnetic phenomena. The discovery that the velocity of electro-magnetic waves is the same as that of light waves is at least circumstantial evidence that the same medium transmits both.

I suppose we all hope that some time we shall succeed in attributing to this medium such further qualities that it will be able to enlarge its scope and take in the work of gravitation.

The mechanical hypothesis has not always taken this dualistic form of material atoms and molecules, floating in a quite distinct ether. I think we may regard Boscovich's theory of point-centres surrounded by infinitely extending atmospheres of force as really an attempt to get rid of the dualism, and Faraday's theory of point-

centres with radiating lines of force is only Boscovich's theory in another form. But Lord Kelvin's vortex-atom theory gives us a simplification more easily thought of. Here all space is filled with continuous fluid—shall we say a fluid ether?—and the atoms are mere loci of a particular type of motion of this frictionless fluid. The sole differences in the atoms are differences of position and motion. Where there are whirls, we call the fluid matter; where there are no whirls, we call it ether. All energy is energy of motion. Our visible kinetic energy, $MV^2/2$, is energy in and round the central whirls; our visible energy of position, our potential energy, is energy of motion in the outlying regions.

A similar simplification is given by Dr. Larmor's hypothesis, in which, again, all space is filled with continuous substance all of one kind, but this time solid rather than fluid. The atoms are loci of strain instead of whirls, and the ether is that which is strained.

So, as we watch the weaving of the garment of Nature, we resolve it in imagination into threads of ether spangled over with beads of matter. We look still closer, and the beads of matter vanish; they are mere knots and loops in the threads of ether.

The question now faces us—How are we to regard these hypotheses as to the constitution of matter and the connecting ether? How are we to look upon the explanations they afford? Are we to put atoms and ether on an equal footing with the phenomena observed by our senses, as truths to be investigated for their own sake? Or are they mere tools in the search for truth, liable to be worn out or superseded?

That matter is grained in structure is hardly more than the expression of the fact that in very thin layers it ceases to behave as in thicker layers. But when we pass on from this general statement and give definite form to the granules or assume definite qualities to the intergranular cement, we are dealing with pure hypotheses.

It is hardly possible to think that we shall ever see an atom or handle the ether. We make no attempt whatever to render them evident to the senses. We connect observed conditions and changes in gross visible matter by invisible molecular and ethereal machinery. The changes at each end of the machinery of which we seek to give an account are in gross matter, and this gross matter is our only instrument of detection, and we never receive direct sense impressions of the imagined atoms or the intervening ether. To a strictly descriptive physicist their only use and interest would lie in their service in prediction of the changes which are to take place in gross matter.

It appears quite possible that various types of machinery might be devised to produce the known effects. The type we have adopted is undergoing constant minor changes, as new discoveries suggest new arrangements of the parts. Is it utterly beyond possibility that the type itself should change?

The special molecular and ethereal machinery which we have designed, and which we now generally use, has been designed because our most highly developed sense is our sense of sight. Were we otherwise, had we a sense more delicate than sight, one affording us material for more definite mental presentation, we might quite possibly have constructed very different hypotheses. Though, as we are, we cannot conceive any higher type than that founded on the sense of sight, we can imagine a lower type, and by way of illustration of the point let us take the sense of which my predecessor spoke last year—the sense of smell. In us it is very undeveloped. But let us imagine a being in whom it is highly cultivated, say, a very intellectual and very hypothetical dog. Let us suppose that he tries to frame an hypothesis as to light. Having found that his sense of smell is excited by surface exhalations, will he not naturally make and be content with a corpuscular theory of light? When he has discovered the facts of dispersion, will he not think of the different colours as different kinds of smell—in-

sensible, perhaps, to him, but sensible to a still more highly gifted, still more hypothetical dog?

Of course, with our superior intellect and sensibility, we can see where his hypothesis would break down; but unless we are to assume that we have reached finality in sense development, the illustration, grotesque as it may be, will serve to show that our hypotheses are in terms of ourselves rather than in terms of Nature itself, they are ejective rather than objective, and so they are to be regarded as instruments, tools, apparatus only to aid us in the search for truth.

To use an old analogy—and here we can hardly go except upon analogy—while the building of Nature is growing spontaneously from within, the model of it, which we seek to construct in our descriptive science, can only be constructed by means of scaffolding from without, a scaffolding of hypotheses. While in the real building all is continuous, in our model there are detached parts which must be connected with the rest by temporary ladders and passages, or which must be supported till we can see how to fill in the understructure. To give the hypotheses equal validity with facts is to confuse the temporary scaffolding with the building itself.

But even if we take this view of the temporary nature of our molecular and ethereal imaginings, it does not lessen their value, their necessity to us.

It is merely a true description of ourselves to say that we must believe in the continuity of physical processes, and that we must attempt to form mental pictures of those processes the details of which elude our observation. For such pictures we must frame hypotheses, and we have to use the best material at command in framing them. At present there is only one fundamental hypothesis—the molecular and ethereal hypothesis—in some such form as is generally accepted.

Even if we take the position that the form of the hypothesis may change as our knowledge extends, that we may be able to devise new machinery—nay, even that we may be able to design some quite new type to bring about the same ends—that does not appear to me to lessen the present value of the hypothesis. We can recognise to the full how well it enables us to group together large masses of facts which, without it, would be scattered apart, how it serves to give working explanations, and continually enables investigators to think out new questions for research. We can recognise that it is the symbolical form in which much actual knowledge is cast. We might almost as well quarrel with the use of the letters of the alphabet, inasmuch as they are not the sounds themselves, but mere arbitrary symbols of the sounds.

In this country there is no need for any defence of the use of the molecular hypothesis. But abroad the movement from the position in which hypothesis is confounded with observed truth has carried many through the position of equilibrium equally far on the other side, and a party has been formed which totally abstains from molecules as a protest against immoderate indulgence in their use. Time will show whether these protesters can do without any hypothesis, whether they can build without scaffolding or ladders. I fear that it is only an attempt to build from balloons.

But the protest will have value if it will put us on our guard against using molecules and the ether everywhere and everywhen. There is, I think, some danger, that we may get so accustomed to picturing everything in terms of these hypotheses that we may come to suppose that we have no firm basis for the facts of observation until we have given a molecular account of them, that a molecular basis is a firmer foundation than direct experience.

Let me illustrate this kind of danger. The phenomena of capillarity can, for the most part, be explained on the assumption of a liquid surface tension. But if the subject is treated merely from this point of view it stands alone—it is a portion of the building of science hanging in the air. The molecular hypothesis then comes in to give some explanation of the surface tension, gives, as it were,

a supporting understructure connecting capillarity with other classes of phenomena. But here, I think, the hypothesis should stop, and such phenomena as can be explained by the surface tension should be so explained without reference to molecules. They should not be brought in again till the surface-tension explanation fails. It is necessary to bear in mind what part is scaffolding, and what is the building itself, already firm and complete.

Or, as another illustration, take the Second Law of Thermodynamics. I suspect that it is sometimes supposed that a molecular theory from which the Second Law could be deduced would be a better basis for it than the direct experience on which it was founded by Clausius and Kelvin, or that the mere imagining of a Maxwell's sorting demon has already disproved the universality of the law; whereas he is a mere hypothesis grafted on a hypothesis, and nothing corresponding to his action has yet been found.

There is more serious danger of confusion of hypothesis with fact in the use of the ether; more risk of failure to see what is accomplished by its aid. In giving an account of light, for instance, the right course, it appears to me, is to describe the phenomena and lay down the laws under which they are grouped, leaving it an open question what it is that waves, until the phenomena oblige us to introduce something more than matter, until we see what properties we must assign to the ether, properties not possessed by matter, in order that it may be competent to afford the explanations we seek. We should then realise more clearly that it is the constitution of matter which we have imagined, the hypothesis of discrete particles, which obliges us to assume an intervening medium to carry on the disturbance from particle to particle. But the vortex-atom hypothesis and Dr. Larmor's strain-atom hypothesis both seem to indicate that we are moving in the direction of the abolition of the distinction between matter and ether, that we shall come to regard the luminiferous medium not as an attenuated substance here and there encumbered with detached blocks,—the molecules of matter,—but as something which in certain places exhibits modifications which we term matter. Or starting rather from matter, we may come to think of matter as no longer consisting of separated granules, but as a continuum with properties grouped round the centres, which we regard as atoms or molecules.

Perhaps I may illustrate the danger in the use of the conception of the ether by considering the common way of describing the electro-magnetic waves, which are all about us here, as ether waves. Now in all cases with which we are acquainted, these waves start from matter; their energy before starting was, as far as we can guess, energy of the matter between the different parts of the source, and they manifest themselves in the receiver as energy of matter. As they travel through the air, I believe that it is quite possible that the electric energy can be expressed in terms of the molecules of air in their path, that they are effecting atomic separations as they go. If so, then the air is quite as much concerned in their propagation as the ether between its molecules. In any case, to term them ether waves is to prejudice the question before we have sufficient evidence.

Unless we bear in mind the hypothetical character of our mechanical conception of things, we may run some risk of another danger—the danger of supposing that we have something more real in mechanical than in other measurements. For instance, there is some risk that the work measure of specific heat should be regarded as more fundamental than the heat measure, in that heat is truly a "mode of motion." On the molecular hypothesis, heat is no doubt a mixture of kinetic energy and potential energy of the molecules and their constituents, and may even be entirely kinetic energy; and we may conceivably in the future make the hypothesis so definite that, when we heat a grm. of water 1° , we can assign such a fraction of an erg to each atom. But look how much pure hypothesis is here. The real superiority of the work measure

of specific heat lies in the fact that it is independent of any particular substance, and there is nothing whatever hypothetical about it.*

Another illustration of the illegitimate use of our hypothesis, as it appears to me, is in the attempt to find in the ether a fixed datum for the measurement of material velocities and accelerations, a something in which we can draw our co-ordinate axes so that they will never turn or bend. But this is as if, discontented with the movement of the earth's pole, we should seek to find our zero lines of latitude and longitude in the Atlantic Ocean. Leaving out of sight the possibility of ethereal currents which we cannot detect, and the motions due to every ray of light which traverses space, we could only fix positions and directions in the ether by buoying them with matter. We know nothing of the ether, except by its effects on matter, and, after all, it would be the material buoys which would fix the positions and not the ether in which they float.

The discussion of the physical method, with its descriptive laws and explanations, and its hypothetical extension of description, leads us on to the consideration of the limitation of its range. The method was developed in the study of matter which we describe as non-living, and with non-living matter the method has sufficed for the particular purposes of the physicist. Of course only a little corner of the universe has been explored, but in the study of non-living matter we have come to no impassable gulfs, no chasms across which we cannot throw bridges of hypothesis. Does the method equally suffice when it is applied to living matter? Can we give a purely physical account of such matter, likening its motions and changes to other motions and changes already observed, and so explaining them? Can we group them in laws which will enable us to predict future conditions and positions? The ancient question never answered, but never ceasing to press for an answer.

Having faith in our descriptive method, let us use it to describe our real attitude on the question. Do we, or do we not, as a matter of fact, make any attempt to apply the physical method to describe and explain those motions of matter which on the psychical view we term voluntary?

Any commonplace example—and the more commonplace the more is it to the point—will at once tell us our practice, whatever may be our theory. For instance, a steamer is going across the Channel. We can give a fairly good physical account of the motion of the steamer. We can describe how the energy stored in the coal passes out through the boiler into the machinery, and how it is ultimately absorbed by the sea. And the machinery once started, we can give an account of the actions and reactions between its various parts and the water, and, if only the crew will not interfere, we can predict with some approach to correctness how the vessel will run. All these processes can be likened to processes already studied—perhaps on another scale—in our laboratories, and from the similarities prediction is possible. But now think of a passenger on board who has received an invitation to take the journey. It is simply a matter of fact that we make no attempt at a complete physical account and explanation of those actions which he takes to accomplish his purpose. We trace no lines of induction in the ether

connecting him with his friends across the Channel, we seek no law of force under which he moves. In practice the strictest physicist abandons the physical view, and replaces it by the psychical. He admits the study of purpose as well as the study of motion.

He has to admit that here his physical method of prediction fails. In physical observations one set of measurements may lead to the prediction of the results of another set of measurements. The equations expressing the laws imply different observations with some definite relation between their results, and if we know one set of observations and that definite relation we can predict the result of the other set. But if we take the psychical view of actions we can only measure the actions. We have no independent means of studying and measuring the motions which preceded the actions, we can only estimate their value by the consequent actions. If we formed equations, they would be mere identities with the same terms on either side.

The consistent and persistent physicist, finding the door closed against him, finding that he has hardly a sphere of influence left to him in the psychical region, seeks to apply his methods in another way by assuming that if he knew all about the molecular positions and motions in the living matter, then the ordinary physical laws could be applied and the physical conditions at any future time could be predicted. He would say, I suppose, with regard to the Channel passenger, that it is absurd to begin with the most complicated mechanism, and seek to give a physical account of that. He would urge that we should take some lower form of life where the structure and motions are simpler, and apply the physical methods to that.

Well, then, let us look for the physical explanation of any motion which we are entitled from its likeness to our own action to call a voluntary motion. Must we not own that even the very beginning of such explanation is as yet non-existent? It appears to me that the assumption that our methods do apply, and that purely physical explanation will suffice to predict all motions and changes, voluntary and involuntary, is at present simply a gigantic extra-polation, which we should unhesitatingly reject if it were merely a case of ordinary physical investigation. The physicist when thus extending his range is ceasing to be a physicist, ceasing to be content with his descriptive methods in his intense desire to show that he is a physicist throughout.

Of course we may describe the motions and changes of any type of matter after the event, and in a purely physical manner. And as Professor Ward has suggested, in a most important contribution to this subject which he has made in his recently published "Gifford Lectures" ('Naturalism and Agnosticism,' "The Gifford Lectures," 1896-98, vol. ii., p. 71), where ordinary physical explanations fail to give an account of the motions, we might imagine some structure in the ether, and such stresses between the ether and matter that our physical explanations should still hold. But, as Professor Ward says, such ethereal constructions would present no warrant for their reality or consistency. Indeed they would be mere images in the surface of things to account for what goes on in front of the surface, and would have no more reality than the images of objects in a glass.

If we have full confidence in the descriptive method, as applied to living and non-living matter, it appears to me that up to the present it teaches us that while in non-living matter we can always find similarities, that, while each event is like other events, actual or imagined, in a living being there are always dissimilarities. Taking the psychical view—the only view which we really do at present take—in the living being there is always some individuality, something different from any other living being, and full prediction in the physical sense, and by physical methods is impossible. If this be true, the loom of Nature is weaving a pattern with no mere geometrical design. The threads of life, coming in we know not

* This risk of imagining one particular kind of measure more real than another, more in accordance with the truth of things, may be further illustrated by the common idea that mass-acceleration is the only way to measure a force. We stand apart from our mechanical system and watch the motions and the accelerations of the various parts, and we find that mass-accelerations have a certain significance in our system. If we keep ourselves outside the system and only use our sense of sight, then mass-acceleration is the only way of describing that behaviour of one body in the presence of others which we term force on it. But if we go about in the system and pull and push bodies, we find that there is another conception of force, in which another sense than sight is concerned,—another mode of measurement much more ancient and still far more extensively used, the measurement by weight supported. Each method has its own range; each is fundamental in that range. It is one of the great practical problems in physics to make the pendulum give us the exact ratio of the units in the two systems.

where, now twining together, now dividing, are weaving patterns of their own, ever increasing in intricacy, ever gaining in beauty.

CORRESPONDENCE.

THE MELTING-POINT OF HYDROGEN.

To the Editor of the Chemical News.

SIR,—The value, about 16.7° C. (abs.), is given by Prof. Dewar for the melting-point of hydrogen in his recent important communication to the British Association, as reported in the CHEM. NEWS, vol. lxxx., p. 132.

A simple calculation shows that a value near to this, viz., 16.768° C. (abs.) is, within narrow limits, a common measure of the melting-points of the family of alkali-metals of which hydrogen is the first member. Thus, taking the determinations given in Roscoe and Schorlemmer's "Chemistry," latest edition, p. 56—

	M.P. (abs.)		16.768		Diff.
H	c. 16.7 (Dewar)	X			
Li	453	27	= 452.73		-0.27
Na	368.6	22	= 368.89		-0.29
K	335.5	20	= 335.36		-0.14
Rb	311.5	18.5	= 310.20		-1.3
Cs	299.5	18	= 301.82		+1.3
—	c. 273	17.5	= 293.44		

c. 293 is the melting-point for the unknown alkali-metal (A.W.c. 223.7) next succeeding to Cs, independently arrived at by a graphical treatment of the melting-points of the elements in a manner similar to that employed for the A.V.'s (*Journ. Am. Chem. Soc.*, xx., No. 12). This graphical treatment clearly demonstrates an interrelation between the A.V.'s, M.P.'s, and B.P.'s of the elements, and in view of the figures given above the question may be asked whether the melting-points of the alkali-metals are not simple multiples of the melting-point of hydrogen. Also, taking 0.086 (Dewar) as the maximum density of liquid hydrogen (= A.V. 11.6), the A.V.'s of the same metals are (but only approximately) simple multiples of this hydrogen value.—I am, &c.,

THOMAS BAYLEY.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 9, August 28, 1899.

Velocity of Detonation of Acetylene.—MM. Berthelot and Le Chatelier.—The authors have studied the velocity of propagation of the detonation of acetylene under different pressures and with other varying conditions. This investigation is interesting, both from the point of view of the theory of propagation of physico-chemical reactions in gases, and also from the point of view of the rules of employment of this gas for illuminating purposes. The gas was contained in horizontal glass tubes about 1 metre long and of diameter between 2 and 6 m.m. It was introduced under pressures varying between 5 and 36 atmospheres, and was found to contain 98 per cent of acetylene. The gas was fired electrically, a small piece of fulminate being used, and the registration of the phenomena was made by the photographic method, which method gives an exact record of all the phases—at least, in so far as the gas remains luminous.

No. 10, September 4, 1899.

This issue contains no chemical matter.

MISCELLANEOUS

Merchant Venturers' Technical College, Bristol.—*Chemistry and Metallurgy.*—Principal, Professor Julius Wertheimer, B.Sc., F.C.S., &c., assisted by Messrs. G. P. Darnell-Smith, B.Sc., &c., H. A. M. Borland, A.R.C.S., H. R. Tutton, F. B. Gatehouse, and W. H. Collier. Physics: Professor A. Philip, B.Sc., and W. G. Hibbins, A.I.E.E., assisted by Messrs. H. E. U. Roberts, W. F. Gibson, and James H. Brinkworth. The Laboratories of this Department are open during the Term on every weekday as a School of Practical Chemistry, Analysis, and Assaying, to students of either sex. They include the Junior Laboratory (for 40 students working at one time), Senior Laboratory, Gas Analysis Room, Balance Room, Combustion Room, Store Rooms, and Metallurgical Laboratory. The training in this department is intended to fit students to become professional chemists, to prepare them for medical or pharmaceutical examinations in Chemistry, to instruct them in the branches of Applied Chemistry required in Manufactures and Agriculture, and to train them in practical Metallurgical processes, especially Assaying. Special facilities will be given to students wishing to undertake research work approved by the Principal; and the courses provide completely for the Preliminary Scientific Examination (M.B.), and for the Examinations in Chemistry for the B.Sc. degree of the University of London. The three years' course at this College in the subjects of Theoretical and Practical Chemistry, Theoretical and Practical Physics, and Elementary Mathematics is accepted by the Council of the Institute of Chemistry as satisfactory evidence of the training of candidates for the Associateship of the Institute, provided the details in each case be certified by the Professors. Certificates of Proficiency in Assaying will be given to students who complete a course of not less than two years' work in the Metallurgical Department, and pass satisfactorily the College Examinations in the Theory and Practice of Assaying. The annual fee of £10 10s. secures (in addition to the use of either or both Laboratories) permission to attend the Lectures in Physics and Mathematics as well as Chemistry, and to use the Physical Laboratory and the Engineering Workshop. Twelve of the students of the College were successful at the last Intermediate B.Sc. Examination of the University of London, and one obtained First Class Honours and two Second Class Honours in Chemistry. The College Evening Classes, available to persons of either sex, will commence on Monday, October 2nd.

On the Chlorinised, Bromised, and Nitrated Derivatives of the Phenetidines, as well as on some Azoic Colouring-matters derived from them.—F. Rierdin and F. Düring.—The authors have endeavoured to decide what is the influence of the respective groups NH_2 , NO_2 , and also the group NH_2 and Cl or Br on the shade of the azoic colouring-matters obtained with the chlorinised, brominised, and nitrated derivatives of the phenetidines. With this object they prepared a number of derivatives, the full description of the preparation and properties of which, as well as a description of their derivatives and the determination of their constitutions, will be found in the *Archives des Science Physiques et Naturelles*, vol. vii., No. 4, p. 201. These bases were utilised either for the production of colouring-matters for fibre treated with β -naphthol, or for the preparation of certain azoic colours; in particular, those derived from salicylic acid, from 1:4-naphtholsulphonic acid of the salt R, from G-amidonaphtholsulphonic acid, and from chromotrope. The result of the experiments shows that, with the chlorised and bromised derivatives, the derivative $\text{C}_6\text{H}_3.\text{OC}_2\text{H}_5.\text{NH}_2.\text{NO}_2$ 1:2:4 gives a much deeper tint than the corresponding derivatives containing Cl or Br in the place of NO_2 .—*Bulletin de la Soc. Chim. de Paris*, Series 3, vol. xxi., No. 7.

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DAVID LEWIS, Treasurer.

Treasurer's Chambers, 20, York Place,
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THE CHEMICAL NEWS.

VOL. LXXX., No. 2080.

NOTE ON THE ACTION OF LIGHT UPON METALLIC SILVER.*

By Major-General J. WATERHOUSE,
Hon. Sec. of the Royal Photographic Society.

FOLLOWING on the lines of Moser's thermographic observations, it may be asserted that metallic silver is sensitive to light. If cut-out masks be laid upon the surface of silver leaf or foil, silvered glass, or on a Daguerreotype plate and exposed to the sun's rays a visible image ultimately becomes apparent on the metallic surface. The effect may, however, be got in a very much shorter space of time if the partly exposed metal be subjected to mercury vapour, or developed by immersion in an acid solution of a ferrous salt mixed with nitrate of silver. Clear images, hardly as yet to be called pictures, can thus be obtained of a permanent character, so that it may be possible to work the Daguerreotype process without iodising the plate. In fact, the photographic phenomena of the invisible developable image, the visible image, reversal, and the effect of pressure marks can all be illustrated on the plain silver surface.

This at least is a new discovery.

Copper seems to be sensitive in the same way, and doubtless other metals.

Postscript.—To avoid contact, a thin sheet of mica was interposed between the silver plate and mask in most of the experiments without appreciably affecting the result.

ON THE PERMANENCE OF CERTAIN GASES IN THE ATMOSPHERES OF PLANETS.†

By G. H. BRYAN, Sc.D., F.R.S.

IN a paper read before the Nottingham Meeting of the Association, the author discussed the application of the kinetic theory of gases to explain the absence of an atmosphere from the moon's surface. In the present investigation similar methods are applied to the atmospheres of planets, account being taken of the axial rotations of the planets. A test of the permanence or otherwise of different gases in the atmospheres of different celestial bodies at different temperatures has been obtained, and a superior limit has been found for the rate at which any planet would lose any gas by the molecules flying off from its atmosphere. To interpret this limit in the simplest possible form, the author has calculated the number of years which would have to elapse in various cases before the quantity of gas lost would be equivalent to that contained in a layer one centimetre thick, covering the surface of the earth. For simplicity absolute temperatures of 200°, 300°, 400°, 500°, and 600° have been chosen—i.e., Centigrade temperatures of -73°, 27°, 127°, and so forth.

In the case of terrestrial hydrogen the loss in question would occupy 84,000,000,000 years at temperature -73°, 600,000 years at -23°, and 222 years at 27° C.

For helium on the earth's surface, the corresponding numbers are 3.5×10^{10} years at -73°, 3×10^{10} or 30 trillion years at 27°, 84,000,000,000 years at 127°, 600,000 years at 227°, and 222 years at 327°.

* Read before the British Association (Section B), Dover Meeting, 1899.

† Read before the British Association (Section A), Dover Meeting, 1899.

For vapour of water on Mars, the figures are 1.2×10^{13} years at -73°, 1.9×10^{16} , or 19 thousand billion years at 27°, 2,400,000,000 years at 127°, 43,000 years at 227°, and 106 years at 327°.

The removal of a layer of air 1 c.m. in thickness from the surface of the earth would only mean a lowering in the average barometric pressure of $\frac{1}{13600}$ of a m.m., roughly. Suppose then that the afore-mentioned gases were present in the respective atmospheres in sufficient quantity to produce pressures comparable with one atmosphere, and assume that a fall of 1 m.m. in the average height of the barometer is the least secular change that could be detected; the above-mentioned intervals of time would have to be multiplied by 13,600 roughly, in order to give the numbers of years in which the escape of the respective gases could be detected by a barometer.

The only possible conclusions from these results are—

1. That helium could exist permanently in our atmosphere at ordinary temperatures.
2. That watery vapour could exist permanently in the atmosphere of Mars at ordinary temperatures.
3. That if helium once existed in appreciable quantities in the earth's atmosphere, it must have escaped when the earth was far hotter than at present.
4. That a similar conclusion holds good on the supposition that Mars once possessed, but has now lost, vapour of water as a constituent of its atmosphere, the temperature-limit at which the loss ceased to be appreciable being, however, lower than for terrestrial helium.
5. That hydrogen, on the other hand, may escape to an appreciable extent from the earth's atmosphere even at ordinary temperatures.

In Dr. Johnstone Stoney's paper it was assumed that helium would escape from the earth's atmosphere, and the author deduced that water could not exist on Mars. Dr. Stoney assumed a temperature of -66° C. in his investigations. It will be seen that the present conclusions for such low temperatures are contrary to Dr. Stoney's hypothesis.

WATER AND SEWAGE EXAMINATION RESULTS.*

REPORT OF THE COMMITTEE APPOINTED TO ESTABLISH A UNIFORM SYSTEM OF RECORDING THE RESULTS OF THE CHEMICAL AND BACTERIAL EXAMINATION OF WATER AND SEWAGE.

THE Committee beg to report as follows;—That it is desirable that results of analysis should be expressed in parts per 100,000, except in the case of dissolved gases, when these should be stated as cubic centimetres of gas at 0° C. and 760 m.m. in 1 litre of water. This method of recording results is in accordance with that suggested by the Committee appointed in 1887 to confer with the Committee of the American Association for the Advancement of Science with a view to forming a uniform system of recording the results of water analysis (*Brit. Assoc. Report*, 1889).

2. The Committee suggest that in the case of all nitrogen compounds the results be expressed as parts of nitrogen over 100,000, including the ammonia expelled on boiling with alkaline permanganate, which should be termed albumenoid nitrogen. The nitrogen will therefore be returned as—

1. Ammoniacal nitrogen from free and saline ammonia.
2. Nitrous nitrogen from nitrites.
3. Nitric nitrogen from nitrates.
4. Organic nitrogen (either by Kjeldahl or by combustion, but the process used should be stated).
5. Albumenoid nitrogen.

* Read before the British Association (Section B), Dover Meeting, 1899.

The total nitrogen of all kinds will be the sum of the first four determinations.

The Committee are of opinion that the percentage of nitrogen oxidised—that is, the ratio of 2 and 3 to 1 and 4—gives sometimes a useful measure of the stage of purification of a particular sample. The purification effected by a process will be measured by the amount of oxidised nitrogen as compared with the total amount of nitrogen existing in the crude sewage.

In raw sewage and in effluents containing suspended matter it is also desirable to determine how much of the organic nitrogen is present in the suspended matter.

In sampling, the Committee suggest that the bottles should be filled nearly completely with the liquid, only a small air-bubble being allowed to remain in the neck of the bottle. The time at which a sample is drawn, as well as the time at which its analysis is begun, should be noted. An effluent should be drawn to correspond as nearly as possible with the original sewage, and both it and the sewage should be taken in quantities proportional to the rate of flow when that varies (*e.g.*, in the emptying of a filter-bed).

In order to avoid the multiplication of analyses the attendant at a sewage works (or any other person who draws the samples) might be provided with sets of twelve or twenty-four stoppered $\frac{1}{2}$ Winchester bottles, one of which should be filled every hour or every two hours, and on the label of each bottle the rate of flow at the time should be written. When the bottles reach the laboratory quantities would be taken from each proportional to these rates of flow and mixed together, by which means a fair average sample for the twenty-four hours would be obtained.

The Committee at present are unable to suggest a method of reporting bacterial results, including incubator tests, which is likely to be acceptable to all workers.

THE TEACHING OF SCIENCE IN ELEMENTARY SCHOOLS.*

THE progress in the teaching of science in elementary schools which was noted in the last report of your Committee has been more than maintained in so far as the number of scholars receiving instruction is concerned. Table A, made up from the return issued by the Education Department, gives the figures for the scientific class subjects, and for English by way of comparison. It will be remembered that for the eight years preceding the Code of 1890, English was obligatory as a class subject if any such subject was taken in the school. The placing it merely on a level with the other subjects had the effect of reducing the number of departments in which English was taken from 20,304 in 1889-90 to 19,825 in 1890-91, while in the same years the number of departments taking Elementary Science rose from the almost nominal figure of 32 to 173. The table shows the progress from that time onwards. It will be observed that there is an extraordinary increase in Object Lessons, which it was pointed out last year would be the case owing to the giving of Object Lessons in the three lower standards being made obligatory after September 1, 1896. The full effect of this change has hardly yet appeared. The return for 1897-98 should show a figure almost equal to the total number of departments. This ascendancy of Object Lessons is fully capable of explaining the decrease in Elementary Science, and does not necessarily involve any lessening of the child's knowledge of Nature. It is rather a question of nomenclature than anything else, in some schools the

object lessons course in the lower standards being still registered under the name of Elementary Science.

The number of departments in "schools for older scholars" for the year 1897-98 was 23,043, all but two of which took one or more class subjects. But History was taken in 5780 departments, and needlework (as a class subject for girls) in 7252 departments, and sundry minor subjects in 972, making, with the other four subjects of the table, a total of 68,534. This shows an average of very nearly three class subjects to each department, but it must be borne in mind that the same subject is not always taken in all the standards, in which case three or more class subjects will appear in the return for a single department.

It has been previously remarked that "the increased teaching of scientific specific subjects in the higher standards is the natural consequence of the greater attention paid to natural science in the lower part of the schools." Table B shows that such is the actual result. It may be noted that every one of these specific subjects shows an actual increase; and the totals indicate an increase of more than 20,000, a larger rise than has been recorded in any previous year.

In last year's report the number of scholars in Standards V., VI., and VII. was estimated at 615,000. The Government returns, in the form in which they are now presented, enable your Committee to make a much more precise estimate; and it now appears that the number of scholars, including the Ex-VII., must have been about 650,000. This figure would give 25.3 per cent as the proportion examined in these specific subjects as compared with the number of children qualified to take them, and the table below has been altered accordingly. The mean number of such scholars for the year 1897-98 is 693,242, which will give 26.6 per cent as the proportion of actual to possible students; but it should be remembered that many of the children take more than one subject for examination.

The following table gives the percentage for each year since 1882, and shows that the great depression which characterised several years has been succeeded by a gradual and steady rise:—

1882-83	..	29.0 per cent	1890-91	..	20.2 per cent
1883-84	..	26.0	1891-92	..	19.7
1884-85	..	22.6	1892-93	..	20.2
1885-86	..	19.9	1893-94	..	20.9
1886-87	..	18.1	1894-95	..	22.7
1887-88	..	16.9	1895-96	..	24.2
1888-89	..	17.0	1896-97	..	25.3
1889-90	..	18.4	1897-98	..	26.6

The Returns of the Education Department given above refer to the whole of England and Wales, and are for the school years ending with August 31. The statistics of the London School Board are brought up to the year ending with Lady Day, 1899. They also illustrate the great advance that has been made in the teaching of Elementary Science, including Object Lessons, as a class subject. (Table C).

The work under the Evening Continuation Schools Code continues to progress, as will be seen by the following table, which gives the number of scholars taking scientific subjects in the year 1897-98 compared with those for the previous year. (See Table D).

The differences represent a total increase of 19,698, which is equivalent to 18.4 per cent. The only actual decreases are in Elementary Physics and Chemistry, Mechanics, Agriculture, and Navigation. It may be remarked that it is rather the practical than the theoretical subjects which are receiving less attention. The Mathematical subjects are still advancing rapidly, and so are Elementary Physiography and the Science of Common Things. The cognate subjects of Hygiene and Ambulance are evidently rising in popular favour. The same may be said of Horticulture. It would be interesting to know the relative proportions of young men and young women in

* Report of the Committee, consisting of Dr. J. H. Gladstone (Chairman), Professor H. E. Armstrong (Secretary), Professor W. R. Dunstan, Mr. George Gladstone, Sir John Lubbock, Sir Philip Magnus, Sir H. E. Roscoe, Professor A. Smithells, and Professor S. P. Thompson. Read before the British Association (Section B), Dover Meeting, 1899.

TABLE A.

Class subjects—Departments.	1891-92.	1892-93.	1893-94.	1894-95.	1895-96.	1896-97.	1897-98.
English.. .. .	18,175	17,394	17,032	16,280	15,327	14,286	13,456
Geography	13,485	14,256	15,250	15,702	16,171	16,646	17,049
Elementary Science	788	1,073	1,215	1,712	2,237	2,617	2,143
Object Lessons	—	—	—	—	1,079	8,321	21,882

TABLE B.

Specific subjects—Children.	1891-92.	1892-93.	1893-94.	1894-95.	1895-96.	1896-97.	1897-98.
Algebra	28,542	31,487	33,612	38,237	41,846	47,225	53,081
Euclid	927	1,279	1,399	1,468	1,584	2,059	2,471
Mensuration	2,802	3,762	4,018	5,614	6,859	8,619	10,828
Mechanics	18,000	20,023	21,532	23,806	24,956	26,110	27,009
Animal Physiology	13,622	14,060	15,271	17,003	18,284	19,989	22,877
Botany	1,845	1,968	2,052	2,483	2,996	3,377	4,031
Principles of Agriculture	1,085	909	1,231	1,196	1,059	825	870
Chemistry	1,935	2,387	3,043	3,850	4,822	5,545	6,978
Sound, Light, and Heat	1,163	1,168	1,175	914	937	1,040	1,155
Magnetism and Electricity	2,338	2,181	3,040	3,198	3,168	3,431	3,905
Domestic Economy	26,447	29,210	32,922	36,239	39,794	45,869	51,259
Total	98,706	108,434	119,295	134,008	146,305	164,089	184,464

TABLE C.

Class subjects—Departments.	1890-1.	1891-2.	1892-3.	1893-4.	1894-5.	1895-6.	1896-7.	1897-8.	1898-9.
Elementary Science	11	113	156	183	208	246	364	322	310
Object Lessons	—	—	—	—	—	—	—	442	657

TABLE D.

Science subjects.	Number of scholars.	
	1896-97.	1897-98.
Euclid	1,036	1,525
Algebra	7,467	9,996
Mensuration	27,388	29,966
Elementary Physiography	3,712	4,807
Elementary Physics and Chemistry	3,135	2,902
Domestic Science	—	117
Science of Common Things	10,910	13,874
Chemistry	5,658	6,590
Mechanics	1,365	1,129
Sound, Light, and Heat	726	813
Magnetism and Electricity	3,834	3,967
Human Physiology	5,865	6,237
Hygiene	3,179	4,062
Botany	692	763
Agriculture	2,355	2,300
Horticulture	1,001	1,354
Navigation	68	37
Ambulance	9,086	13,030
Domestic Economy	19,565	23,271
Totals	107,042	126,740

these latter classes, but the Government returns do not supply this information. The only one of these subjects reserved exclusively for women is Domestic Economy. Domestic Science, as distinguished from the preceding, has only recently been formulated, and the first-fruits are only beginning to make their appearance in the column for the latter year. Unlike the day school work, which is largely governed by the requirements of the Education Department, and the preferences of managers and teachers, the Evening Continuation classes are to a great extent regulated by the public local demand, which rather seems to be for a continuation of the studies which have been begun in the Elementary Schools than for those practical subjects which are specially provided for by the Technical Instruction Act.

The London School Board have just passed a series of resolutions on the subject of the teaching of science in their schools, and amongst others that "Experimental Science instruction was desirable for girls as well as for boys:"—that "scholars of about Standard IV. should

have an opportunity of doing some practical work themselves, such as linear (or other) measurement:"—and that "where some definite science is taught in the upper part of the school, the teaching of Experimental Science in the lower part of the school should lead up to it." The extension of the teaching of Science in the Board Schools has necessitated the Science demonstrators giving more and more attention to the preparing of the ordinary teachers for giving practical instruction in Science in their classes. These teachers have usually obtained certificates for one or more sciences under the Science and Art Department, but that does not necessarily qualify for the practical teaching of science according to modern views. Hence the need of the preparation above referred to. It would seem desirable that only those teachers who have some interest in, or aptness for, experimental work should be selected for this kind of training, and after having become thus qualified, they should be assigned, as far as possible, to this particular work. To carry this out more thoroughly, the board have decided "that Experimental Science classes for teachers be started under the Board in the autumn," and "that there be courses of Pedagogical Lectures to secure the practical teaching of Elementary Science, confined to teachers who have reached a certain standard of scientific knowledge of the subject on which the lectures are given."

It is to be hoped that under the newly constituted Education Department far more attention will be given than heretofore to improving the conditions under which science is taught in schools. Especially is it important that attention should be paid to the practical training of pupil teachers in the elements of scientific method. The time given to such work is altogether inadequate at present. But in some ways too much is often attempted, and from this point of view your Committee think it desirable to recall attention to the recommendations in the last paragraph of their report for 1897, as up to the present time no action has been taken by the Education Department.

The South-Western Polytechnic, Chelsea.—The Day College for Men, the Day College for Women, and the Evening Classes commenced on September 25th. Full particulars of all these classes may be obtained from the Secretary, Manresa Road, Chelsea.

SYNOPSIS FOR A DISCUSSION ON "LAWS OF SUBSTITUTION, ESPECIALLY IN BENZENOID COMPOUNDS."*

By Prof. HENRY E. ARMSTRONG, F.R.S.

1. In considering the formation of substitution derivatives from benzene and allied compounds, it is necessary to account for the very distinct behaviour of substances containing compound acid radicles (*i. e.*, radicles which in combination with OH form acids), which yield a large proportion of meta- derivative, whilst compounds containing other radicles yield ortho- and para-, and little, if any, meta- derivative. But no absolute distinction can be drawn, as much depends on the condition under which the change takes place, a considerable proportion of meta- derivative being obtained, for example, from aniline by nitrating it in presence of a large excess of sulphuric acid.

2. In the case of an amino- compound, it is possible to trace the action through a series of stages. Thus in sulphonating aniline, the sulphate first undergoes conversion into sulphamic acid, and this is converted into either ortho- or para- sulphonic acid, according to the conditions under which it is placed.

3. The process involved in the passage of sulphamic into sulphonic acid may be regarded as one of *isomeric change*—*i. e.*, it may be supposed that the SO_3H group wanders from one part of the molecule to another, without leaving the system and temporarily entering into some other form of combination.

In favour of this view is the fact that sulphonic acids are produced by the action of a sulphite on nitro- compounds under conditions under which the occurrence of independent sulphonation of the nucleus is, to say the least, unlikely; it is scarcely possible to doubt that in such cases the sulphamate is an intermediate product, as phenyl- hydroxylamine is converted into phenyl- sulphamic acid by the action of sulphur dioxide (Bamberger).

4. The possibility of isomeric change occurring in such a case cannot be denied in view of the fact that secondary nitrosamines, for example, are converted into para- nitrosamines by the action of acids, and of the many similar cases of change which have been brought to light in recent years by Bamberger, Hantzsch, and others.

In many such cases the change is so complete that it is impossible to believe that the radicle which wanders is first displaced from the molecule, and that the compound which is formed from it then enters into action with the molecule from which it was derived: for example, that in the case of the nitrosamines referred to the nitroso- group is split off in the form of nitrous acid, which then acts so as to form a para- nitroso- derivative; or, again, that when parido- orthonitrophenetol is formed on nitrating orthiodophenetol the iodine becomes separated from the molecule and then attacks it afresh.

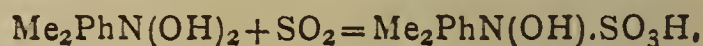
Moreover, bearing in mind the extreme readiness with which change takes place, for example, in the case of the formation of parachloracetanilide from the compound PHNClAc or of sulphanilic from phenylsulphamic acid, it is difficult to believe that the formation of the one compound is not a necessary stage in the formation of the other: the readiness with which the substituted benzenoid compound is obtained is so great that it is to be expected that both compounds would be formed together if they were independent products of the action of a single agent—just as, in fact, often happens in the case of para- and ortho- compounds.

5. It is very difficult to form any precise conception of the manner in which such "isomeric changes" are brought about. Something more than a mere interchange of position of the radicles is involved in them: some agent intervenes; but the operation of the agent is easily

overlooked, as only a minute quantity suffices in many cases, the action being "fermentative" in character.

6. Very probably the peculiar structure of benzene and the tendency to pass from the centric to an ethenoid form and back again is the determining cause of the change; may be the function of the transforming agent is to bring about the change from the centric to a highly unstable ethenoid form, and the radicles change places at the moment that the agent is extruded from the compound and the system relapses into the centric form. A rough parallel is afforded by the well-known game of chairs, in which chairs are provided for all but one of a number of players; at a given signal all rise up and join their seatless companions, and then at another signal all seek to obtain seats: at this moment players are somewhat guided in their choice of places by the desire of certain couples to sit together; eventually the seats are again all occupied, but the order of the occupants is different, and as before one remains out.

7. Only primary and secondary amines can furnish sulphamic acids, and their formation is necessarily impossible in the case of tertiary amines; but it can scarcely be doubted that these are converted in the first instance into a sulphonated ammonium compound. The formation of *o.* and *p.* dimethylanilinesulphonic acids from dimethylaniline oxide and sulphur dioxide cannot well be otherwise interpreted, and in fact is so formulated by Bamberger:—



8. Bamberger assumes that the formation of para- sulphonic acid from sulphamic acid is preceded by that of the ortho- acid, but in view of the stability of the ortho- acid this is improbable; it is to be expected that it would in a large measure persist under the conditions which, as a matter of fact, entail the production of only the para- acid. Thus, if acetanilide be carefully sulphamated, the product poured on to ice, and the solution then boiled, only sulphanilic acid is obtained; but if the solution of sulphamic acid in sulphuric acid be allowed to absorb water very gradually at a low temperature, a large proportion of ortho- acid is formed.

Apparently the ortho- acid is formed from the sulphamic acid if the sulpho- group be, as it were, let down gently; otherwise the para- acid is produced.

When the ortho- is converted into the para- acid by heating it with sulphuric acid, probably it is first hydrolysed, and sulphamic acid is then formed, and this in turn undergoes conversion into para- acid.

9. Whatever the changes involved in the production of ortho- and para- compounds, the nitrogen in amino- compounds clearly exercises both an attractive and a directive influence.

The nature, and more particularly the degree, of its influence depends, in a remarkable manner, on the nature of its immediate associates; hydrogen especially exercises an altogether peculiar influence on the course of substitution.

Nitrogen *per se* has little attractive or directive power, compounds such as azobenzene and diazobenzene bromide manifesting a singular inertness in presence of substituting agents; and it would seem that the more the influence of the hydrogen in amines is counteracted and the basic properties of the nitrogen neutralised, the more nearly do aminoid compounds generally approximate in their behaviour to simple azo- derivatives.

10. But not only does nitrogen cease to be attractive and directive when deprived of hydrogen and neutralised; it apparently even acquires inhibiting powers.

Thus dimethylanilineparasulphonic acid exchanges only a single atom of hydrogen for bromine, and the SO_3H group is displaced with difficulty by the further action of bromine. This behaviour is in striking contrast with that of sulphanilic acid, which is very readily converted into tribrom- aniline by the mere addition of bromine to its aqueous solution.

The effect of acid radicles is even more striking, and

* Read before the British Association (Section B), Dover Meeting, 1899.

somewhat different in character from that exercised by alkyls: thus when a single molecular proportion of bromine is added to a solution of acetylsulphanilic acid, less than half the acid is converted into the monobrominated acid; a major proportion simply exchanges the sulphonic group for bromine. Benzoylsulphanilic acid in like manner yields a mixture of monobrominated acid and parabromobenzanilid.

The stability of the brominated acid from dimethylanilinesulphonic acid is perhaps accounted for—on the assumption that the attack proceeds from the nitrogen atom—by the fact that it forms a relatively stable dibromide. In the case of the monacetylated acid, on the other hand, it may be supposed that the hydrogen in the amino-group is initially displaced, and that the bromine “wanders out” from this position partly into the ortho- and partly into the para-position.

11. When the conditions under which meta-derivatives are formed from amines are considered, it is clear that they are such as to favour the neutralisation of the basic properties of the amines, and to prevent the displacement of aminoid hydrogen.

The nitration of aniline in presence of excess of sulphuric acid may be taken as an example. A major proportion of the molecules being present as sulphate, the excess of nitric acid to the azo-radicle, and therefore to the system, is prevented: consequently no nitramine is formed, and a necessary stage in the formation of both *o*- and *p*-nitro-derivative is eliminated and their production prevented. On the other hand, as the action takes place at a low temperature, and nitric acid is present in its most concentrated form—perhaps as anhydride, in large measure—the conditions are such as to favour the attack of the benzenoid portion of the molecule, but only in the meta-position, the ortho- and para-positions being in a measure protected, owing to the inhibitive influence exercised by the fully saturated azo-radicle.

Although the basic properties of aniline are much reduced by the introduction of acetyl, acetanilid is still sufficiently basic to be attractive of nitric acid, and it therefore undergoes conversion into nitramine, and subsequently into ortho- and para-nitro-derivative.

Benzanilid being far less basic, is only very partially acted upon in this manner; the benzenoid portion of the molecule is therefore preferred for attack, and consequently a considerable number of molecules become meta-nitrated.

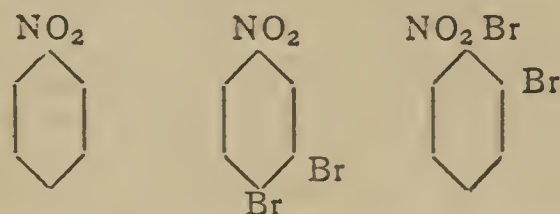
Dimethylaniline is converted entirely into para-acid when sulphonated by ordinary sulphuric acid at about 180°, or by chlorosulphonic acid; but when carefully sulphonated by fuming acid it yields a large proportion of meta-acid. Doubtless, in this latter case, the conditions correspond to those pictured in the case of benzanilid undergoing nitration. That the formation of meta-acid is a consequence of the sulphate undergoing sulphonation, and is not merely due to the use of the more powerful agent SO₃, clearly follows from the fact that so powerful an agent as SO₃HCl converts dimethylaniline only into para-acid.

The behaviour of acetanilid and benzanilid towards forming sulphuric acid is precisely similar to their behaviour towards nitric acid—the former gives only *o*- and *p*-acid, the latter a considerable proportion of meta-acid. Probably both are initially converted into sulphamic acid; but the acid formed from the latter being less prone to undergo isomeric change, it becomes in part meta-sulphonated.

12. In the case of compounds other than amines which afford meta-derivatives, it may be supposed that the radicle is both unattractive and “ortho-para inhibitive,” and that consequently opportunity is given for the attack to become concentrated upon the benzenoid portion of the molecule in the meta-position.

As in such cases some proportion of *o*- and *p*-compound is usually obtained, it is necessary to assume—if the radicle be regarded as altogether unattractive—that

the benzenoid portion of the molecule is open to attack at several points; indeed, this may be more or less true of all compounds. Thus it may be supposed that when nitrobenzene is brominated two compounds are initially formed, thus:—



The 1:2 compound being a very minor product, but little ortho-compound is eventually obtained, and, owing to the unattractive and inhibitive influence exercised by the NO₂ group, bromine is chiefly separated from the para-position of the 3:4 compound; consequently but little para-derivative is formed.

13. The phenols in many ways closely resemble the amines in their behaviour towards substituting agents. The hydrogen in association with the oxygen clearly plays an important part; in fact, the extreme activity of phenols is probably, in large measure, due to the presence of hydrogen in the extra-benzenoid radicle, as in the case of the amines, but the part which the hydrogen plays cannot at present be at all clearly made out.

By displacing the hydroxylic hydrogen by alkyls, effects are produced very similar to those observed in the case of amines. Thus phenol-parasulphonic acid, like sulphanilic acid, at once exchanges two atoms of hydrogen for bromine, and then quite readily exchanges the SO₃H group for bromine. But the acids obtained by introducing methyl, ethyl, or benzyl in place of the hydroxylic hydrogen yield only monobrominated acids, which on further treatment exchange the SO₃H group for bromine; and this action takes place only partially, as a large proportion of the acid directly exchanges the SO₃H group for bromine, a monobrominated compound being formed, just as in the case of acetyl- and benzoyl-sulphanilic acid.

Benzoyl appears to exercise a very remarkable inhibitive effect, as preliminary experiments show that benzoylated phenolparasulphonic acid remains unattacked by bromine under conditions which involve the conversion of the unbenzoylated acid into tribromo-phenol.

It may therefore be supposed that oxygen in phenols, being possessed of residual affinity, exercises an influence on substitution similar to that which nitrogen exercises in amines; and as it has no basic qualities, it is difficult, if not impossible, to deprive it of its activity, and consequently of its para-ortho-orienting power: hence it is that phenols do not yield meta-derivatives. Should conditions be discovered which will make it possible to hold the activity of oxygen in check, it will probably be found possible to directly prepare meta-phenolic derivatives.

14. Sulphur, whilst resembling oxygen, apparently has a still stronger inhibitive influence. Thus phenyl ethyl thio-ether may be para-sulphonated without difficulty, but para-bromophenyl ethyl thio-ether is not sulphonated either by sulphuric or by chlorosulphonic acid, although the corresponding oxygen compound is very readily acted on.

15. The behaviour of halogen derivatives may be correlated with that of phenols, or rather with that of their ethers, especially in view of the existence of compounds such as phenyl iodosochloride, PhICl₂. On the assumption that the residual affinity of iodine was satisfied in this compound, it appeared not improbable that it might furnish a meta-sulphonic acid. It is sulphonated without difficulty, but the product is highly chlorinated, and its nature has yet to be ascertained.

16. The hydrocarbons homologous with benzene are the most difficult group to discuss. The paraffinyl radicle certainly exercises a directive effect; whether it is in any way attractive is open to question. Bearing in mind the inactivity of the paraffins, it is difficult to believe that the radicles derived from them are possessed of sufficient

activity to account for the striking readiness with which the homologues of benzene are acted upon in comparison with benzene. The introduction of hydrogen radicles seems, in fact, to produce a fundamental modification in the centric complex, the behaviour of hydrocarbons such as mesitylene being ethenoid rather than benzenoid; and from this point of view it seems probable that the derivatives of benzenoid hydrocarbons are formed more in accordance with the process formulated in paragraph 12.

The fact that when the paraffinyl radicle undergoes chlorination or oxidation, for example, the attack, as a rule, takes place at the point of attachment is proof that, if not itself attractive, it immediately adjoins the centre of attraction; and it is possible that initially some change takes place in which both radicles are involved.

OXIDATION IN THE PRESENCE OF IRON.*

By HENRY J. HORSTMAN FENTON, M.A., F.R.S.

THE remarkable influence which iron exerts upon the oxidation of certain organic substances was first pointed out by the author in 1876 in the instance of tartaric acid. This observation has since been fully investigated, and has led to an extensive study of the behaviour of various other substances under similar conditions of oxidation and of the resulting products (Fenton, *CHEM. NEWS*, 1876, xxxiii., 190; 1881, xliii., 110; *Trans. Chem. Soc.*, 1894, 899; 1895, 48 and 774; 1896, 546; 1897, 375; 1898, 71 and 472, &c. Fenton and Jackson, 1899, 1 and 575; Cross and Bevan, 1898, 463; 1899, 747; Morrell and Crofts, 1899, 786; Martinon, *Bull. Soc. Chim.*, 1885, ii., 23, 196; Ruff, *Ber.*, 1898, 1573; 1899, 550.

The peculiar advantage of the method consists in the fact that the extent of oxidation may be regulated, and consequently that it is often possible to obtain products of limited oxidation which cannot be prepared in any other way.

Hydrogen peroxide is the most efficient oxidising agent for the purpose, although others may sometimes be substituted. The iron, which is essential to the process, must in almost all cases be present in the ferrous condition; its proportion, however, bears little if any relation to the yield.

With regard to the general nature of the oxidation products, it may be observed that in the case of tartaric acid the change may be represented as a removal of the two non-hydroxylic hydrogen atoms; in the polyhydric alcohols the (primary) CH_2OH groups are attacked in preference to the (secondary) CHOH groups, whilst in certain carbohydrates the CHOH group adjacent to an aldehyde group appears to be oxidised; the aldehyde group itself is remarkably resistant. In the benzenoid compounds H is usually replaced by OH, and a similar behaviour would appear to obtain in the furfurane derivatives. In all cases it might be assumed that the initial result is the replacement of H by OH, tartaric acid, for example, being supposed to give, in the first instance, trioxysuccinic acid.

The part played by the iron in these changes is still a matter for discussion. In a previous note (*Proc. Chem. Soc.*, 1898) a provisional theory was proposed, in which it was suggested that the ferrous iron first replaces non-hydroxylic hydrogen and is subsequently oxidised; and it is certainly remarkable that in the case of every substance found to be sensitive to this reaction, non hydroxylic hydrogen is present, associated in almost every case with alcoholic hydroxyl.

With a view of throwing further light upon the general nature of this oxidation process, the author is at present studying a variety of substances of typical constitution,

and the following is a brief account of results which have recently been obtained with certain acids:—

Tartronic acid gives a large yield of mesoxalic acid. The hydrazone of the latter acid separates at once on the addition of phenylhydrazine hydrochloride, and it is probable that the process may be found advantageous for the preparation of the free acid, especially as the production of tartronic acid has been much simplified (*Trans. Chem. Soc.*, 1898, 72). This transformation has not hitherto been effected, although the converse operation—the reduction of mesoxalic to tartronic acid—is well known.

Lactic acid, in a similar manner, yields pyruvic acid, but the operation requires especial care.

Glyceric acid, when oxidised in the same way, produces a substance having strong reducing properties, and which gives an intense violet colour with ferric salts in the presence of alkalis. On treatment with phenylhydrazine acetate an osazone is produced which crystallises in golden needles, melts at 203° , and gives a beautifully crystalline sodium salt and pyrazolon. It appears to coincide in every way with the osazone of oxypyruvic acid, $\text{C}_{15}\text{H}_{14}\text{N}_4\text{O}_2$, which was obtained by Nastvogel from dibromopyruvic acid (*Annalen*, 248, 85), and by W. Will from the product of the action of soda on collodion wool (*Ber.*, 1891, 400). The substance produced in the present case may therefore be (1) oxypyruvic acid, (2) the semi-aldehyde of tartronic acid, or (3) the semi-aldehyde of mesoxalic acid.

Malic Acid.—Judging from previous results, it was to be expected that this substance would yield oxal-acetic acid, and it is possible that such may be the result in the first instance, since, on treatment of the product with sulphuric acid, a certain amount of pyruvic acid is obtained. If, on the other hand, the product be treated with phenylhydrazine acetate, a substance is obtained which crystallises in golden prisms, melts at $216-218^\circ$, and gives crystalline sodium and potassium salts.

The above-mentioned products are being fully investigated, and the results will shortly be published.

The author wishes to express his thanks to Mr. H. O. Jones, B.Sc., for the valuable assistance which he is giving in this portion of the work.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING AUGUST 31ST, 1899.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, September 11th, 1899.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 208 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from August 1st to August 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 208 samples examined by us during the month, all were found to be clear, bright, and well filtered.

* Read before the British Association (Section B), Dover Meeting, 1899.

The drought in the Thames Valley during August has been less severe than during the two previous months. The total rainfall at Oxford in August was 1.80 inches, the average for the last thirty years being 2.32 inches. This makes a deficiency of only 0.52 inch, compared with deficiencies of 1.06 inches for June and 1.36 inches for July. The total deficiency for the year is now 3.63 inches, or 22.6 per cent.

Our bacteriological examinations of 382 samples have given the results recorded in the following table; we have also examined 49 other samples, from special wells, stand-pipes, &c., making a total of 431 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	410
New River, filtered (mean of 76 samples) ..	12
Thames, unfiltered (mean of 26 samples) ..	2269
Thames water, from the clear water wells of eight Thames-derived supplies (mean of 206 samples)	31
Ditto ditto highest	289
Ditto ditto lowest	0
River Lea, unfiltered (mean of 26 samples) ..	863
River Lea, from the East London Company's clear water well (mean of 26 samples) . . .	12

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

JAMES DEWAR.

ON THE ESTIMATION OF CHLORINE, BROMINE, AND IODINE WHEN MIXED.

By J. BOUGAULT.

A CONSIDERABLE number of methods have been proposed for the separation one from the other of chlorine, bromine, and iodine, with a view to their separate estimation. These methods, fairly practicable in the case of iodine, are much more delicate of application when we have to deal with the separation of chlorine from bromine, on account of the so closely allied chemical affinities of these two elements. Further, text-books generally recommend as the best an indirect method which comprises the three following operations:—1. Precipitation by nitrate of silver and weighing the mixed precipitate; 2, Conversion of the whole of the argentic precipitate into chloride of silver and weighing the chloride of silver formed; 3. Separation of the iodine, either by precipitation with chloride of palladium, or by setting it free by means of an oxidising agent (MnO_4K , CrO_4K , NO_2H , &c.), and removing it by means of sulphide of carbon. In the case of the presence of two halogens only, it is evident that the two first operations will suffice.

I thought it would be possible to advantageously substitute, for the second operation, reduction of the mixed precipitate of the haloid salts of silver by reduction with zinc and sulphuric acid, and weighing the reduced silver. This modification rests, as will be seen, on a well-known reaction; but the simplicity of its execution, the accuracy of the results, and the fact—which has surprised me not a little—of not finding it described anywhere, have caused me to call attention to it.

The following is the best method of procedure:—

We must first make quite certain that the zinc used is completely soluble in dilute sulphuric acid; granulated zinc fulfilling this condition, described as chemically pure, can be obtained commercially.

We then weigh very exactly a quantity of argentic precipitate of from 0.5 grm. to 1 grm. in a small precipitating glass, and add about 50 c.c. of dilute sulphuric acid (50 grms. SO_4H_2 in 500 grms. of water). We then take a quantity of chemically pure zinc about equal to that of

the argentic precipitate, and add it in small portions of 0.15 grm. to 0.2 grm., waiting for one portion to be almost dissolved before adding the next. In a very short time the whole of the argentic precipitate is brought to the state of metallic silver; we allow the excess of zinc to become completely dissolved (this is absolutely indispensable); we must make certain that this takes place by making sure that the solution contains no solid particle giving rise to a disengagement of gas, no matter how feeble; any particle of zinc would thus be easily detected. To make still more certain, it is as well to leave the mixture for a few hours with occasional stirring. When all the zinc is dissolved, we filter and wash with distilled water.* The precipitate is dried in the oven, calcined in a tared crucible, and weighed; the increase in weight of the crucible, less the weight of the ash of the filter, gives the weight of the reduced silver.

I have carried out this operation on chemically pure chloride, bromide, and iodide of silver prepared specially for verifying the accuracy of the process, and obtained the following results:—

	Theory.
0.521 grm. AgI gave me 0.2392 of silver.	0.2394
0.545 " AgCl " 0.4104 "	0.4102
0.678 " AgBr " 0.3898 "	0.3894
0.3825 " AgCl } " 0.4698 "	0.4698
0.3960 " AgI }	

I would add that I have had occasion to apply this method to the estimation of chlorine and of iodine in substances containing from 40 to 50 per cent of iodine, with only 3 to 6 per cent of chlorine; the results obtained were very satisfactory.—*Journ. de Pharm. et de Chim.*, Series 6, vol. x., No. 1.

DETECTION AND COLORIMETRIC ESTIMATION OF SMALL QUANTITIES OF IODINE IN ORGANIC MATTERS.

By PAUL BOURCET.

THE material in which we wish to search for iodine is, according to its nature, finely chopped up or powdered, it is then moistened with a dilute solution of potash completely free from iodine, then dried in the oven at 100°. The dried mass is again finely powdered, then melted with potash free from iodine in an iron crucible, or, better still, a nickel one.†

The fusion ended, the mass is allowed to cool and is then exhausted with boiling distilled water until the filtered washings are no longer sensibly alkaline. The solution thus obtained is reduced by evaporation to one-half its original volume. To the cold solution we add, very gradually, pure sulphuric acid diluted with five times its weight of distilled water, taking care to avoid all heating, and, if necessary, even cooling down the vessel in which the saturation is effected. When the solution is neutral, a few drops of a solution of potash free from iodine are added to make it slightly alkaline, and then, with continued stirring, one-half its volume of alcohol at 95° is slowly added. The greater part of the sulphate of potash is thus precipitated in the state of a fine powder, which is drained on a filter-pump and washed with alcohol at 30 per cent, which carries off the mother-liquors

* The filtered liquid and the wash waters contain the whole of the hydrochloric, hydrobromic, and hydriodic acids formed during the reaction. By precipitating with nitrate of silver we can recover the argentic precipitate used integrally.

† When we use an iron crucible, we should commence by melting the potash free from iodine, and rinsing the whole of the interior surface of the crucible with the melted potash. We thus remove the small quantity of iodine which iron crucibles may sometimes give up to the potash the first time they are used for such a fusion.

with which it is impregnated. The filtrate is evaporated down to one-third of its original volume, and when cool is treated with alcohol at 90°. A further quantity of sulphate of potash is precipitated; this is drained and washed with alcohol at 30 per cent, as before. By repeating the concentration of the filtrates and their precipitation by alcohol several times, we finally eliminate all, or nearly all, the sulphate of potash, while the iodine—if there is any present—is concentrated in the alkaline liquids soluble in alcohol.

The last solutions thus obtained are evaporated to dryness in a nickel or porcelain crucible, and the residue submitted to gentle heating over the flame to destroy the small quantity of organic matter which might still be present. On cooling, it is taken up with a small quantity of warm distilled water and filtered; it is in the few c.c. of solution thus obtained that the iodine is displaced by nitrous fumes in the presence of sulphide of carbon, and is then estimated colorimetrically according to the method given by MM. Rabourdin and Nicloux.

We are confident by this method we should be able to recover the whole of the iodine added to an organic material nitrated or not, but not iodised.

Thus, for example, taking two samples of sugar free from iodine, each weighing 100 grms., to which $1/30$ th and $2/30$ ths of a m.grm. of iodine in the form of an alkaline iodide had been added, we found, after having treated them both according to the method we have just described, that the residue of the second sample of sugar contained double the quantity of iodine found in the residue of the first, and that colorimetrically the latter agreed with a solution in which we had previously dissolved $1/30$ th of a m.grm. of iodine.

This method of detecting and estimating iodine has enabled us to determine very small quantities of iodine in a certain number of alimentary materials the weights of which varied from 50 grms. to 1 kilogram. Our qualitative and quantitative estimations of the iodine in these substances form the object of another research which we have not yet completed. For the present, as an example, we give the results which we found with various kinds of fish.

	Iodine per kilogram.
M.grm.	
Smoked herring (eggs)	0·8
" " (soft roes)	0·6
Do. (whole)	1·7
Do. (whole)	1·8
Do. (whole)	2·0
Portuguese oysters	1·3
Fresh ray	0·2
Whiting	0·3
Mackerel	0·3
Sardines (salted)	0·6
Gurnet	1·2
Mussels	1·9
Cod (salt).. .. .	1·2
Coal fish (intestines)	2·4
Do. (flesh)	0·9
Shrimps	0·7
Periwinkles	0·75
Eel	0·8
Pike	0·3
Roach	1·2
Gudgeon	0·12
Bream	1·2
Sole	0·8
Salmon (head)	1·4
Salmon trout	0·1
Carp	0·6
Mullet	0·6
Ling	1·2

We have made a large number of other estimations which lead to general deductions which we shall make known later on.—*Bull. Soc. Chim.*, Series 3, xxi., No. II.

ANALYTICAL METHODS FOR DISTINGUISHING BETWEEN NITROGEN OF PROTEIDS AND NITROGEN OF SIMPLER AMIDES OR AMIDO-ACIDS.

By J. W. MALLET,
Professor of Chemistry, University of Virginia.

(Continued from p. 119).

METHODS OF SEPARATING NITROGEN.

A BRIEF notice of several methods of separating nitrogen will afford means of comparison. The phospho-tungstic method which was especially investigated is treated more fully than the others.

Dialysis.

The attempt to separate such proteids as are soluble in water from the simpler amides intentionally mixed with them by applying Graham's method of dialysis was made with no great hope of success. It is, of course, well known that the amorphous proteids in solution exhibit as a class a very small degree of diffusive mobility, while the crystallisable, simpler amides diffuse through a porous septum, as of parchment paper, with much greater rapidity. But separation based on this difference can never be complete. Only a part of the more diffusible material can be obtained in the water on the opposite side of the diaphragm from the mixed solution, and that a large part shall be so obtained requires that the volume of water used shall be large as compared with the volume of the solution. Moreover, the absolute volume of the solution itself must be large where amides of but slight solubility—such as tyrosin—are present, in order that they may not be left behind in the undissolved state. But the time required for dialytic separation extends to many hours, or even several days, and during such protracted exposure to the air and to common atmospheric temperature weak solutions of the proteids readily undergo chemical change. Again, it is to be remembered that the peptones, classed with the proteids, are diffusible in much higher degree than natural proteid material prior to its exposure to the action of the digestive fluids. This fact has well-known physiological importance in its bearing on the preparation of proteid food for absorption from the alimentary canal, but in analysis it tends to confound the particular group of the peptones with the simpler amides. In the recovering from weak solutions of small quantities of dissolved substances by the evaporation of large amounts of water, further chemical change of the substance recovered is likely to vitiate the results.

Nevertheless, some twenty or more experiments were carried out with dialysers made from the tubes of parchment paper which can now be bought in Germany. Cylinders of about 6 inches long were cut from these tubes, and closed at one end by thin glass, carefully tested as to freedom from holes, and immersed in water contained in ordinary glass beakers. A fairly clean separation was obtained of leucin, aspartic acid, and creatin, from solutions to which had been added egg or serum albumen, the diffusate being in each case evaporated at a moderate temperature over the water-bath, and the residue weighed. But the process of diffusion was inconveniently slow, and less satisfactory results were obtained when the dialysed solution was made more complex by the addition of other substances.

Subsequently the writer's attention was attracted by the paper of Charles J. Martin (*Journ. Physiol.*, 1896, xx., 364—371), on the use for a like separation of a Pasteur filter in the pores of which a film of silicic acid has been deposited, the filtration being brought about under pressure. It has been practicable to make only two or three experiments in this way. The method is decidedly promising, but it seems more likely to be useful in the purification of substances in quantity than as a process of analysis. With small quantities of material it

can hardly be made available for regular laboratory work in connection with nutrition investigations. It involves the same difficulty as any other form of dialysis in cases in which the proteoses and peptones are present.

Interaction with Nitrous Acid.

It was hoped that by varying the conditions of experiment with this reagent some characteristic differences of behaviour might be observed as regards the evolution of elementary nitrogen.

The most advantageous mode of producing nitrous acid in definite amount was found to consist in bringing together, along with the material to be acted upon, pure silver nitrite and a hydrochloric acid solution of known strength. The action took place in a glass flask of about 100 c.c. capacity, closed by a stopper through which passed through the long neck of a cylindrical funnel holding about 60 c.c., the neck having an interior diameter of but 1 m.m., and separated from the wider cylindrical reservoir by a well-ground glass stopcock. There also passed through the same stopper the stem of a thermometer reading to one-tenth of 1 degree with accuracy, a small tube with stopcock for the introduction of gas to displace the air of the apparatus, and a second small tube to carry off the nitrogen evolved. The capacity of the flask was carefully gauged with the tubes and thermometer in position and the stopper inserted to a marked depth in the neck, so that after the introduction of any known volume of solid or liquid material a simple subtraction would give the volume of gaseous matter remaining included. A gas-measuring cylinder, connected with the flask by a tube of very small bore and immersed in water in a larger cylinder which could be raised or lowered, provided for collecting and measuring the evolved nitrogen. The flask was supported in a water-bath, so that it could be heated or cooled at pleasure.

In order to give time for action upon the organic material under experiment, and to keep down to conveniently small limits the evolution of nitrogen dioxide, it was found important to work with the nitrous acid in a sufficiently diluted condition. With the same object in view it was found desirable to raise the temperature of the flask very gradually. In carrying out an experiment the particular amidic or proteid material was finely pulverised, weighed off, and introduced into the flask, either in the dry state or with as little recently boiled water as possible, and with the necessary amount of silver nitrite, as a fine crystalline powder. This powder was contained in a small, thin, glass cylinder, which could be easily upset in order to mix its contents with the other materials in the flask. A current of nitrogen gas was next run through the flask until all air was expelled. In the case of substances dissolving in water with difficulty the flask was now allowed to stand closed for some time to permit of solution taking place. Communication was established with the gas-measuring cylinder, and the proper quantity of standard hydrochloric acid, made by diluting very strong aqueous acid with boiled water and kept in small well-closed bottles, was gradually introduced through a funnel with capillary bore. Care was taken that no air was admitted. After all action in the cold had ceased the temperature of the flask was gradually raised by means of the water-bath up to a maximum of about 96° or 97° C. As soon as all action was over and the apparatus had cooled down to atmospheric temperature the flask was nearly filled up with recently boiled water, introduced through the capillary funnel, and a small measured volume of nitrogen was run in to displace any remaining nitrogen dioxide. The gas in the measuring cylinder was then treated with oxygen in sufficient excess to dispose of all nitrogen dioxide, and with caustic potash and pyrogallol to remove excess of oxygen. After standing at rest for some time the gas was measured, due allowance being made for the nitrogen present in the flask at first and for the small additional amount afterwards introduced. Of course, the proper corrections for pressure, temperature,

and tension of aqueous vapour, were made in connection with all the measurements of gas, and the quantity of nitrogen obtained was divided by 2, one half being yielded by the organic substance and the other by the nitrous acid.

With a view to guard against the retention of any nitrogen in the form of di-azo derivatives from amides, a moderate excess of hydrochloric acid was used. In the case of kreatinin the results are complicated by the formation of the supposed nitroso-compounds observed by Dessaignes. With several of the proteids the bright yellow colour of the so-called xantho-proteid acid was well-marked, as the consequence, doubtless, of the action in the flask of nitric acid produced by the breaking up of nitrous acid into nitric acid, nitrogen dioxide, and water. Too little is known of the yellow substance formed, Mulder's xantho-proteid acid, to indicate how far its nitrogen comes from the proteid and how far from the nitric acid, or in what direction or to what extent its formation may influence the amount of elementary nitrogen given off. In the case of proteid solutions coagulable by heat, it was manifestly important to allow the action of the hydrochloric acid on the silver nitrite to become complete below the temperature of coagulation, as otherwise silver nitrite was entangled in clots of the coagulating proteid. In some, at least, of these experiments, it seemed probable that a part of the nitrogen dioxide given off, and perhaps of the free nitrogen, was due to the reducing action of the carbon or hydrogen of the organic substance upon nitrous or nitric acid, and not solely to the normal interaction of nitrous acid and the amidogen radicle present.

The process was varied, not only in respect to the temperature applied, but also, within moderate limits, in respect to the pressure on raising or lowering the gas measuring-tube in the water. It was further varied by increasing the proportion of nitrous acid to different extents in excess of the theoretically necessary amount.

In all some fifty or sixty experiments were made. In a number of cases the simpler amidic compounds gave a fair approximation to the quantity of nitrogen theoretically to be expected from them, though even with such substances as leucin, asparagin, and aspartic acid, the results were not as sharp as the claims of Sachsse and Kormann would lead one to suspect. One of the best experiments yielded for aspartic acid 9.57 per cent of nitrogen, instead of the 10.53 per cent actually present. Kreatin did not give one-half of its nitrogen, as has been heretofore recorded as the fact, but a somewhat nearer approach to one-third,—10.19 per cent as against 32.06 per cent,—the probability of which result is indicated by the accepted structure of the molecule. In all cases the proteids gave some nitrogen, but the proportion was much smaller than from the simpler amides, and varied much more with the precise conditions of temperature, pressure, and strength of solution used. In one experiment serum albumen gave but 2.68 per cent, and in another but 2.92 per cent was obtained from hæmoglobin.

On the whole, the indications pointed to the simpler amides and amido-acids being most easily decomposed by nitrous acid, the proteoses and peptones perhaps next, and the proteids proper least. But no differences were observed upon which any useful analytical process of separation or distinction could be based. Experiments made in this way are, moreover, troublesome, and require strict observance of the necessary precautions to avoid error from introduction of air into the apparatus and its action on nitrogen dioxide.

Interaction with Potassium Permanganate in presence of Free Acid or Alkali.

THE writer had not much hope of obtaining useful results by this method, in view of former experience gained in connection with the extended research upon the determination of organic matter in drinking water carried out many years ago for the U.S. National Board of Health,

of which the results were published in the annual report of that Board for 1882. Still, as the work then done was upon extremely dilute solutions, comparable in respect to the amount of organic matter present with natural potable waters, it seemed possible that results not altogether of the same sort might be obtained with solutions of greater concentration. Hence some thirty or forty experiments were made with permanganate strongly acidified with sulphuric acid, and a rather larger number with the same salt after potassium hydroxide had been added in about the same proportion as is usual for the Wanklyn, Chapman, and Smith so-called albumenoid-ammonia process. In the former set of experiments the amount of oxygen withdrawn from the permanganate, and in the latter set the amount of ammonia produced, were determined. In both cases the reactions were carried out at various temperatures up to the boiling-points of the several liquids.

Some difference was observable in the results obtained with the comparatively strong solutions used, such difference being more notable for alkaline than for acid permanganate. But in the main these results only confirmed the conclusions arrived at in the earlier research. The effect of the reagent employed is imperfect, and varies much with the nature of the individual organic materials tested; much, also, with the conditions of the experiment and with the rate at which the action proceeds. No valid evidence is obtained in support of Wanklyn's view that simple and definite fractions of the total nitrogen present are evolved as ammonia on treatment with alkaline permanganate.

Some special difficulties and sources of error already known were re-observed; as, for instance, the continuous evolution of ammonia by boiling many organic substances with alkaline permanganate until distillation has practically brought the contents of the retort to dryness, without all of the nitrogen present having been given off. And some other causes of trouble were noticed; as, for instance, the loss of oxygen given off as such from a strong and acid solution of permanganate on standing in a heated condition irrespective of action on the organic matter present.

The general tenour of the results in the case of the nitrogenous substances treated pointed to more energetic and extensive action of permanganate in alkaline than in acid solution; also to more extensive action on the simpler amidic compounds than on the proteids. But notwithstanding sundry variations of method as to strength of the reagent solutions, proportion of reagent to organic material acted on, temperature, and time of action, no indication was obtained of any valid basis for distinction in analysis between the two classes of nitrogenous material studied.

Interaction with Sodium Hypobromite.

This reaction is so frequently used for the approximate determination of urea (carbamide), while its results with other amides have been so scantily examined and almost no facts bearing on its relation to the proteids have been recorded, that a good deal of interest was felt in examining it somewhat extensively with the two classes of materials which were studied.

The solution of bromine was prepared with 240 grms. of potassium bromide, 200 grms. of free bromine, and enough water to make up a litre. The solution of caustic soda was made with 340 grammes of pure sodium hydroxide to the litre. These solutions were preserved in separate bottles, and equal volumes of the two were mixed just before using. When undiluted the mixture represented 0.1 gm. of originally free bromine to each c.c., and was in most of the experiments used of this strength; but various dilutions were also employed, being made by additions of water in definite amount.

The apparatus with which the reaction was carried out was essentially the same as that adopted for the experiments with nitrous acid, save that the small tube was

omitted which was intended to introduce an inert gas to displace air from the apparatus, this precaution being unnecessary in the hypobromite experiments.

Nearly eighty experiments were made, varying the conditions as to temperature from that of the atmosphere, usually 15° to 20°, up to 96° to 98° C., as to pressure within the limits allowed by the immersion of the gas-measuring cylinder, and as to time from fifteen or twenty minutes up to five or six hours.

In some cases the results obtained were in agreement with those of the few hitherto recorded experiments—as, for instance, aspartic acid gave no nitrogen, as was found to be the fact by Allen and Tankard. In other cases there was disagreement with some of the published statements and confirmation of others. Thus, Allen and Tankard obtained no nitrogen from glycosin (A. H. Allen, "Commercial Organic Analysis," 1896, vol. iii., Part 3, p. 275), and Tankard none from asparagin,* while Oechsner de Coninck reported both these substances as acted on (by sodium hypochlorite) when gently heated, nitrogen gas being evolved (*Comptes Rendus*, 1895, cxxi., 893, 894; *Journ. Chem. Soc. (London)*, 1896; Abstracts, *Org. Chem.*, p. 282). The writer obtained from glycosin 4.2 per cent of nitrogen instead of 18.67 per cent as required by the formula,† and from asparagin 11.12 per cent instead of 18.67 per cent, the amount calculated, taking account of the presence of a molecule of water of crystallisation.

In a number of cases the quantity of nitrogen evolved from an amide or amido-acid of known constitution seemed to represent a simple fraction of the total quantity contained in the material operated on, and it might not unnaturally be suspected, as in some of the cases reported by Allen and Tankard, that one-fourth or one-half to two-thirds of the whole quantity was liberated. Thus in one experiment leucin gave 2.58 per cent of nitrogen instead of 10.69 (calculated), or about one-fourth; in another, kreatin gave 21.96 per cent instead of 32.06 (calculated), about two-thirds; and in another, hypoxanthine gave 18.80 per cent instead of 41.18 (calculated), which might mean one-half—two atoms out of four. But it is not believed there is any more real significance in these approximations to definite fractional parts of the nitrogen being evolved than in the similar approximations to which Wanklyn drew attention in connection with his so-called albumenoid-ammonia process. His conclusions have been shown to be entirely erroneous. Different figures could be obtained from the same materials acted on by varying the conditions of the experiment, and in some cases there was no really sharp ending to the reaction, traces of gas continuing to be slowly given off for hours after the main portion had been collected. Moreover, while our knowledge of the constitution of kreatin would make it not improbable that two atoms of nitrogen out of three should be liberated or two out of four in the case of hypoxanthine, there is no similar ground for any expectation that leucin, containing but one atom of nitrogen in the molecule, should yield one-fourth; or glutamic acid, also with but one atom, should yield something like one-fourth (2.56 per cent instead of 9.52 calculated).

The researches of S. Hoogewerff and W. A. van Dorp have shown that numerous definite products other than elementary nitrogen may be formed by the action of alkaline hypobromites upon amides and amido-acids, especially those containing cyclic nuclei. In several of the writer's experiments—as, for instance, with alinin among the simpler amido-acids, and with a sample of globulin among the proteids—a crystalline residue separated out in the flask on cooling. This residue was not examined further than to determine qualitatively that it contained nitrogen. The proportion borne by the nitro-

* Possibly the solutions were not heated.

† In Watts's "Dictionary of Chemistry," revised edition by M. M. Pattison Muir and H. F. Morley, vol. ii., p. 627, it is stated, on the authority of Denigès (*Comptes Rendus*, cvii., 662), that with sodium hypobromite nitrogen is evolved from glycosin.

gen left in such fixed residual products to that collected as gas evidently varied with the conditions of the particular experiment, as well as with the nature of the substance acted on.

All the proteids and analogous materials treated gave some gaseous nitrogen. For the most part the amount was about two-fifths of the whole amount present; but occasionally a larger proportion, as in one experiment with globulin just about one-half, and in another with myosin about three-fourths. In this last case the action was allowed to go on at a high temperature for a time much longer than usual. The remarks already made in regard to the simpler amidic substances, as to modification of results by variation of the conditions of experiments, fully apply also to the experiments with proteids and their congeners. The lack of sharpness of ending to the reaction was more noticeable with the latter class of materials than with the former.

Although these experiments with alkaline hypobromite were interesting, and occasionally offered points which might repay further investigation, they did not, taken altogether, afford any satisfactory basis for distinguishing in analysis between the classes of materials to be studied in contrast with each other.

(To be continued).

NOTICES OF BOOKS.

The London Water Supply. By ARTHUR SHADWELL, M.A., M.B. (Oxon.), Member of the Royal College of Physicians. London, New York, and Bombay: Longmans, Green, and Co. 1899. Pp. 272.

THE London water supply has attracted considerable attention of late years, more especially since the London County Council commenced its attack on the London water companies nine or ten years ago.

The author has treated his subject in a masterly manner, and has traced the formation and growth of the water companies from their inception many years ago to the present time. He points out very pertinently that "for years the water companies have been a common cock-shy for every kind of ridicule and abuse." Last autumn the newspapers, mostly of a certain political complexion, were full of insults, spiteful innuendoes, and silly sarcasms against the officials of the East London Company, as if they were personally responsible for the existence of the concern, which was established by Act of Parliament before they were born.

Many people think that if they throw enough mud some is sure to stick, and it has been stated so many times that London is abominably served with water, that it is scanty in quantity, bad in quality, and very dear, that we drink "diluted sewage," &c., that doubtless some people think this is all true.

The author has carefully gone into figures of the quantity, quality, and cost of London water as compared with most of the large towns in England. A few of these figures will not be uninteresting. First, with regard to quantity; out of a list of twenty-four of the largest towns in England there are only three, viz., Brighton, Plymouth, and Hull, which have a greater daily supply per head than London. Of the three above-mentioned towns each has an average daily supply of 43 gallons per head, that of London being 38½ gallons; most of the other twenty-one towns have a considerably smaller supply.

With regard to quality, the supplies of so few towns are systematically examined as that of London is, that figures are not easy to procure; but compared with figures obtained from Birmingham and Glasgow, the water from these two model municipalities is seen to contain considerably more organic matter than London water, while the death rate from typhoid in Glasgow is double that of London.

A table given by the author of the cost of the water supply in thirteen of these towns shows that the poorer consumers in London enjoy a very considerable advantage over those in the provinces; the highest charge in London is appreciably lower than the provincial average, while the London average cost is no less than 40 per cent lower than the average provincial figure.

Brighton is the only town, according to the author, which has a distinct advantage over the London water companies; this advantage arises from Brighton being situated immediately under the great chalk downs, which form an enormous natural reservoir.

A word or two with regard to failures in London. There was the general breakdown from frost in 1895, and there were the so-called water famines in the East of London in 1895, 1896, and 1898; these comprise all the failures, real and otherwise, in London. In other great towns in England there have been many failures. Manchester has broken down six times since 1874, Liverpool four times, Bradford eight times, while in 1868 Manchester, Sheffield, Bradford, Halifax, Newcastle, and many other towns suffered severely, but London not at all. During the last twenty-five years the eight London water companies have only actually broken down three times between them, while the eight next largest towns have done so at least thirty times; moreover, whenever there is a breakdown in a municipal supply, such as all these great towns enjoy, with the single exception of Bristol, the ratepayers have not only to put up with the inconvenience, but have also to pay for the repairs.

We have no hesitation in saying that there is no water supply in the world which is looked after with such constant and systematic care as that of London. Over 600 samples a month are examined by the companies' chemists; these samples are taken daily from all the filtering stations belonging to the London water companies, and the slightest abnormal condition at any point is immediately communicated to the company concerned by telephone or telegraph. It is by this constant supervision that the very high character of the London water supply is maintained.

Practical Organic Chemistry; the Detection and Properties of some of the more important Organic Compounds. By SAMUEL RIDEAL, D.Sc. (Lond.), F.I.C., F.C.S. Second Edition. London: H. K. Lewis. Pp. 172.

THE more important tests and reactions of the common organic compounds are collected together in this volume; the most characteristic reactions are distinguished by an asterisk, while a brief summary of the distinctive tests for each group of bodies is also given. As a help to the medical student a list of the *Materia Medica* preparations and organic compounds included in the British Pharmacopœia is also given. In this edition several additional organic substances have been included, as well as a few other compounds of general interest.

The substances dealt with in this volume are the organic acids with the cyanide group; the carbohydrates, including the glucoses, saccharoses, and starches; the organic bases, with the fixed and volatile alkaloids; and neutral substances, such as the alcohols, albumen and gelatin, chloroform, the aldehydes, ethers, &c.

At the end of the book, the order of analyses for the detection and identification of the commoner organic substances is given. The book is well and clearly written, and well adapted for the use of students.

Chemistry for Continuation Schools. By R. L. TAYLOR. Manchester: Thomas Wyatt. 1899. Pp. 52.

THE course of experimental lessons in chemistry contained in these pages was originally intended for teachers in the evening continuation schools of the Manchester School Board; but it has been found to be of great use

when put into the hands of the pupils. The instruction given in this book is essentially elementary, and is intended only for beginners; the descriptions being clear and the experiments simple, we have no doubt but that it will be of great use in the classes for which it is intended.

A Manual of Pharmaceutical Testing for the Man of Business and his Assistants. By BARNARD S. PROCTOR, F.I.C. Second Edition. London: The Chemist and Druggist. 1899. Pp. 192.

THE present edition of this book includes various notes which have been accumulated by the author since the appearance of the first edition in 1891, and up to the time of the publication of the British Pharmacopœia for 1898.

Such directions for testing are given as will, it is hoped, enable any ordinary pharmacist to examine and determine the quality of his chemicals with such reagents, &c., usually found at the dispensing counter. The author has endeavoured to point out the probable impurities which may be present, and it is to these the tests specially apply; adulterations are of course more difficult to detect. We must express some surprise at the inclusion of a chapter on manipulation and apparatus, such as weighing and measuring, specific gravity, precipitates, &c. There is far too great a tendency to include such chapters in books of this class, and we are certainly of opinion that every pharmaceutical chemist would have such knowledge at his fingers' ends.

As for the rest of the book, we have no fault whatever to find; it is well written and arranged, and will be a useful addition to the pharmacist's book-shelf.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., Nos. 10, 11, and 12.

These three numbers contain no matter of chemical interest.

Journal de Pharmacie et de Chimie,
Series 6, Vol. ix., No. 7.

This number contains no matter of chemical interest.

No. 8.

Compounds obtained with the Fatty Aldehyds and Mercuric Sulphate.—G. Denigès.—Already noticed.

Method of Testing for, and the Composition of, Oils of Acetone.—A. and P. Buisine.—Oil of acetone obtained from grease contains only traces of dimethylketone, not more than 5 per cent; it contains at least 90 per cent of compounds with an acetonic function, of which 75 per cent are soluble in water. This portion is formed to a very great extent of ethylmethylketone. Comparative tests have been made with samples of oils of acetone from a factory where the acetone was made by means of pyrolignite of lime; these oils are very different in composition, being much poorer in ketones passing over below 90°, they hardly contain half the quantity of ethylmethylketone that the former ones do, while they are much richer in the higher ketones.

No. 9.

Iodised Sulphur and Iodide of Sulphur.—L. Prunier.—Iodised sulphur is prepared by heating sulphur to about 115 to 120°—that is, to just about melting point—and gradually adding to it an equal quantity of iodine. Stir till the iodine is dissolved and allow to cool; the pro-

duct crystallises completely in a blackish brown mass—which must be kept in well stoppered flasks, as the iodine is very volatile. When reduced to powder, iodised sulphur immediately gives up its iodine to a solution of hyposulphite. There are several iodides of sulphur: the one experimented on was formed by first heating the sulphur to its second fusing-point; a thermometer is then plunged into the mass, which is allowed to cool down to about 200°, when the pasty state is reached; the coarsely-powdered iodine is then gradually added (4 parts of iodine to 1 of sulphur). The combination takes place with considerable energy. When all the iodine is added, the mass is allowed to cool; it, however, always contains iodised sulphur in varying proportions.

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Professor of Chemistry in the University of Tübingen.

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With a Preface by the Author.

*** In preparing a second edition of the translation of Meyer's "Outlines of Theoretical Chemistry," the translators have availed themselves of the second edition of the German, published in 1893, a few years before the death of Lothar Meyer. Whilst the original form has been still retained, they have, by occasional footnotes and appendices, sought to bring the book up to date.

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THE CHEMICAL NEWS.

VOL. LXXX., No. 2081.

SYMBIOSIS.*

By Professor MARSHALL WARD, F.R.S.

Synopsis.

ORIGIN of the idea and of the term. Differences between parasitism and symbiosis.

Lichens, previously regarded as autonomous plants, are shown to be dual organisms, a symbiosis of alga and fungus. Controversy regarding the lichen theory, and establishment of the latter by means of synthetic cultures.

Other cases of symbiosis known previous to 1880. Algæ in the stems of *Gunnera* and the roots of *Cycas*, in the thallus or fronds of *Anthroceras*, and *Blazia*, *Azolla*, *Lemna*, &c.

Extension of the idea of symbiosis: insect fertilisation, epiphytes, &c.

Galls not necessarily due to insects, but may be due to the irritating action of fungi or bacteria. Phytocecidia of the Aleppo pine, &c.

Symbiosis in animals. Green infusoria, hydra, sponges, &c.

Mycorrhiza, the roots of many humus plants curiously swollen and modified owing to the presence of fungi, which do not injure the plant, but link its roots to the decomposing leaves around. Explanation as an instance of symbiosis. Evidence partly anatomical and partly experimental.

"Budding" and "grafting" are processes involving the establishment of a symbiosis.

The nodules on the roots of leguminous plants. Discovery and controversy as to their nature. They contain living bacteroids, which penetrate the root hairs and flourish in the living cells. Universality of these nodules on healthy roots. Hellriegel and Willfarth's cultures, and evidence as to the fixation of nitrogen. Laurent and Schloesing's proof that nitrogen is fixed from the air.

The leguminous nodules a case of symbiosis, comparable to galls.

Other instances not yet explained. Nodules on the roots of *Funcus*, *Myrica*, and other plants.

Symbiotic fermentations. All natural fermentations mixed. Pure cultures and the importance of synthetic cultures.

Kephir, the ginger-beer plant, and other instances of symbiotic ferments. Decomposition of cellulose. Nitrifying and denitrifying organisms. The direct alcoholic fermentation of starch by the simultaneous action of two fungi.

Return to the idea of symbiosis. Necessity of limiting the term. Antibiosis (antagonism). Metabiosis. Difficulty of distinguishing in given cases. Hypothetical considerations, and importance of further investigations.

Particular Cases.

The above may be accepted as affording general headings under which the subject of symbiosis might be treated.

For the purposes of this discussion I proceed to consider some special cases, and limit myself—as requested to do—to certain aspects of symbiotic fermentations.

Several cases of symbiosis among bacteria are now known. Apart from numerous instances of temporary association between pathogenic micro-organisms and animals such as earth-worms, rats, flies, ticks, and mosquitoes,

and which disseminate their germs and infect cattle, sheep, horses, and men, reminding us of the transference of the spores of *Botrytis* by bees, which carry this parasite with the pollen and infect the stigmas of bilberries with the parasite; or which act the part of intermediate hosts to the disease germs, much as certain pond snails do to the liver-fluke of sheep, we now know several cases of symbiosis between two species of bacteria or of fungi, or between a bacterium and a fungus, each symbiont being incapable of carrying on alone the work which the symbiotic association is able to perform—a point which is essential to the definition of symbiosis in the narrower sense, *i.e.*, the co-operation of two associated organs to their mutual advantage.

A striking example is afforded by certain bacteria concerned in the destruction of cellulose in ponds, bogs, rivers, &c. Van Senus found that a certain anaërobic bacterium, resembling, if not identical with, Van Tieghem's *B. Amylobacter*, though incapable of dissolving cellulose by itself, can do so if associated with another bacterium, also incapable of itself attacking cellulose. *B. Amylobacter* can ferment pectose compounds, and is thus capable of isolating cells one from another, but cellulose is not attacked by it.

Van Senus believed that the one bacillus destroys certain products of fermentation excreted by *B. Amylobacter*, which inhibit its cellulose-fermenting powers.

I may remark here that, if a sound potato, rhizome, or other underground organ is placed in water and the air exhausted as completely as possible, I almost invariably find its cellulose walls destroyed in a few days by a mixture of bacteria, and with the symptoms found in many kinds of "wet rot." There is no reason to believe that these organs would rot if merely wet and not deprived of air, since they lie in ordinary soil—even moist soil—for weeks or months, with plenty of water in their tissues, and respire oxygen, as is well known. The presumption is that the anaërobic conditions set up in the experiment described favour certain forms of soil bacteria, such as Van Senus worked with, and enable them to co-operate in the destruction of the cell walls.

An even more remarkable example is given by Winogradsky, who found that the anaërobic bacterium known as *Clostridium Pasteurianum* is able, if supplied with abundance of dextrose and protected from the access of oxygen, to fix atmospheric nitrogen. In the cultures, and presumably in the soil, the *Clostridium* was found to work when protected by a mantle of aerobic bacteria. In fact, the nitrogen-fixing *Clostridium* was working in the meshes of the oxygen-consuming species, and forming gelatinous flocks like the well-known grains of kephir, or of ginger-beer plant.

Yet another striking instance of symbiotic association has recently been given by Omeliansky. In experiments on nitrification at Bonn, the assertion had been made that the nitrifying organisms—*i.e.*, the bacteria known to oxidise ammonia to nitrous acid, and nitrous acid to nitric acid—could be grown and made to do their specific work in media containing proteids or other organic nitrogenous bodies. Now this was directly contradictory of the experience of Warrington, Winogradsky, and other workers, who had found that one great peculiarity of these nitrifying organisms is that they refuse to grow on such media; they are incapable of using organic nitrogen. Several workers then showed that the Bonn observers had inadvertently employed mixtures of two or more species, and Omeliansky undertook a critical investigation of the whole subject, and has put forward the following explanation of the tangle:—

If *Nitrosomonas*—the bacterium which oxidises ammonia to nitrous acid—and *Nitrobacter*—the bacterium which further oxidises nitrous to nitric acid—be sown together or separately on a medium containing organic nitrogen, no growth or change occurs.

But if a bacterium capable of decomposing the organic nitrogenous medium, *e.g.*, *Bacillus ramosus*, is added to

* Read before the British Association (Sections B and K), Dover Meeting, 1899.

the above-mentioned *Nitrosomonas* and *Nitrobacter*, the associated three organisms are able to carry out all the processes and complete the cycle of nitrification. That is to say *B. ramosus* breaks down the gelatin and ammonia is formed; this is then oxidised to nitrous acid by *Nitrosomonas*, and the nitrous acid is further oxidised to nitric acid by the *Nitrobacter*.

If *B. ramosus* and *Nitrosomonas* only are sown together, then only nitrous acid is formed, because the latter organism is only capable of carrying the oxidation the one stage.

If *B. ramosus* and *Nitrobacter* only are used, then only ammonia is formed, because the latter organism cannot oxidise ammonia.

If we try to imagine the working of this association of organisms in the soil, and bear in mind the frequent co-existence and action of the de-nitrifying bacteria which Gayon and Dupetit, Giltay and Aberson, Warington and others, have familiarised us with, a glimpse is obtained of the very complex symbioses which may be concerned in the circulation of nitrogen in Nature. Moreover, some of these de-nitrifying bacilli appear to be anaërobic, and can only work in the surface soil if protected from the access of oxygen—say, by an associated aërobic bacterium.

Another interesting case is the following:—Perdix a few years ago isolated from water an anaërobic bacterium which converts starches into sugars, which with the aid of a yeast can be fermented, the whole process going on in association.

Other cases of symbiotic associations of bacteria exist among the forms concerned in the reductions of sulphates and the oxidation of sulphuretted hydrogen, the iron bacteria, &c.; but I propose to mention only one or two further examples, taken from the true fungi.

Symbiotic associations of fungi are probably common, but only a few cases are as yet established, and these principally among the ferment-fungi.

Van Laer has called attention to the symbiotic co-existence of two yeasts in many beers, explaining certain peculiar after-fermentations as due to the action of one yeast acting on the medium improved for it by the other.

The Japanese have long been in the habit of brewing a peculiar fermented liquor known as rice-wine, or saké. Rice grains are steamed, and when cool are infected with a mould fungus now known as *Aspergillus Oryzæ*. When the rice is quite mouldy, at which time it emits a peculiar odour like that of pine-apples, the starch is found to be rapidly turning to sugar, under the action of a diastatic enzyme secreted by the fungus.

This decomposing rice is then placed in water and exposed to the action of a yeast, which rapidly ferments the sugar, and the alcoholic saké results.

So closely is the yeast associated with the *Aspergillus*, that, in practice, the alcoholic fermentation commences soon after the enzyme of the *Aspergillus* begins to hydrolyse the starch of the rice, and for some time a controversy existed as to whether the yeast was not really part of the life-history of the *Aspergillus*. Several observers have now shown, however, that we have here a striking case of symbiosis.

On reviewing these examples, we shall find that very different degrees of association of the organisms are to be met with.

At the one end of the series we find two organisms merely associated for a short time, *e.g.*, bacilli and worms, bees and botrytis-spores, and, so far as we may speak of symbiosis at all in these cases, it is merely temporary or disjunctive.

At the other end of the series we have a close permanent combination of the two organisms working in unison, *e.g.*, the lichens and Winogradsky's *Closterium* with its protective mantle of aërobic bacteria; also the ginger-beer plant and kephir.

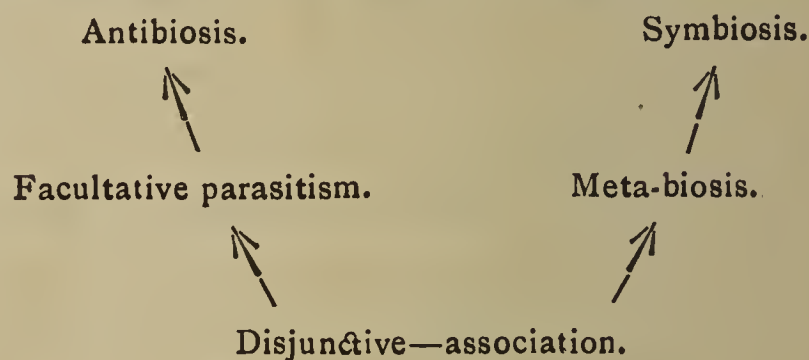
But between these extremes it is possible to find all stages, the half-way house being met with in cases such

as the saké ferment, where the *Aspergillus* evidently prepares the way for the Yeast.

It has been proposed to apply the term *Metabiosis* to such cases.

It must not be forgotten that there are extremes in the other direction, where one of the two associated organisms is injuring the other, as exemplified by many parasites, but these cases I leave out of account here. This state of affairs has been termed *Antibiosis*.

It seems not impossible that the biological relationships of these cases one to another could be shown thus:—



The Physiology of Symbiosis.

It will be an interesting exercise to see if we can get any further glimpses into the physiology of the phenomenon of Symbiosis.

When we come to enquire as to the processes which lead to enhancement of the functional activity of one organism by another living symbiotically with it, the matter presents many difficulties; for it is at the outset quite obvious that many things are possible, and soon becomes evident that a tangle of complexities lies before us, as always in the inter-relations between associated biological units. We need go no further than the examination of the possibilities in the inter-relations between a weed and a cultivated plant, or between two trees in a forest, for illustrations of this truth.

Confining attention for the moment to closely associated symbionts, such as those composing a lichen, the ginger-beer plant, or a clump of symbiotic bacteria or fungi, researches have made it practically certain that the provision of definite food-materials by the one symbiont for the other may be an important factor; *e.g.*, an alga supplies a fungus with carbo-hydrates, or a fungus converts starch into the fermentable sugars which the associated yeast needs. In other cases the advantage derived is one of protection from some injurious agent—*e.g.*, the aërobic bacterium prevents the access of oxygen to the anaërobic one. But there is evidence which suggests that mere nutrition or protection is not the only, or even the principal, factor involved. It is well known that the products of fermentative actions are frequently poisons, and we all know of cases where such poisonous excreta of living cells act as stimuli to other living cells, if supplied to them in minimal doses and very gradually: I need only instance the effects of tobacco or alcohol on man, in illustration of this.

Several observers have shown that in presence of a particular food-substance the living cell is stimulated to produce and excrete a particular enzyme, while the substitution of another food stimulates the organism to excrete a totally different enzyme.

Now let us see if there is any evidence to support the hypothesis that some such stimulative action is exerted by one symbiont on another. To a certain extent we find such in the remarkable vigour and large size of the algal cells in a lichen as compared with the same cells living an independent life, and in the persistent zone of brilliant green and often hypertrophied cells of leaves in which certain fungi are living, the gigantic cells of the nodules on leguminous roots in which the bacteroids are living, and many other cases; but since it is impossible to say how far these are cases of merely enhanced nutrition, we will pass them by and seek for other instances.

One of the earliest I can find is Hugo Schulz's demon-

stration, in 1888, that minute quantities of poisons—such as corrosive sublimate, iodine, iodide of potassium, bromine, arsenious acid, chromic acid, sodium salicylate, or formic acid—when added to yeast in 10 per cent grape-sugar solution, immediately raise the fermentative activity of the organism, as measured by the amount of carbon-dioxide evolved. Effront, in 1894, showed that hydro-fluoric acid acts similarly on yeasts, butyric ferments, and *mycoderma*, and, later, that the same is true of formaldehyde, salicylic acid, picric acid, &c.

What looks like another case in point is Johannsen's results of experiments with seeds, buds, &c., treated with ether or chloroform; respiration is increased, and the whole course of metabolism so altered that in some cases buds of flowers can be stimulated to open long before their normal period.

The results obtained by Farmer and Waller with carbon-dioxide, which was found to induce an initial acceleration of the movement of the protoplasm in *Elodea*, may be a further instance.

Pfeffer has recently called attention to a still more remarkable instance—that it is possible, by etherising the living cells of *Spirogyra* to alter the type of nuclear division from *mitotic* (indirect) to *a-mitotic* (direct). Massart had shown that callus, the hypertrophied tissue developed under stimulation by mites, fungi, exposure to air, &c., is formed of cells which divide with *a-mitotic* nuclear division; and other cases occur. But it is even more to the point for my purpose that Gerassimoff, in Pfeffer's laboratory, found *Spirogyra* driven to *a-mitotic* division by associated bacteria and other organisms, which he regards as a case of symbiosis.

Now it may be regarded as certain that if a cell can be thus stimulated to alter the details of so fundamental and complex a morphological process as its cell-division by the action of associated organisms, the metabolic activities of its protoplasm are being driven into very different channels from the normal, and many physiological processes must be affected.

Of course I am here raising questions which concern the border-line between health and disease, and much investigation is still required as to the meaning of these matters; but I ought to add that, according to Pfeffer, the etherised cells can be again restored to their normal state if the traces of anæsthetic are washed out, and those familiar with Kleb's experiments on other algæ will appreciate the significance of this one with *Spirogyra*.

However feeble the evidence may be, we can at least say, then, that there is some evidence in support of the hypothesis that one symbiont may stimulate another by excreting some body which acts as an exciting drug to the latter—just as truly as certain drugs act as stimulants to some cell or organ of a higher animal, and no doubt in a fundamentally similar manner. It will be noted that such drugs are frequently excreta from vegetable cells.

But there is another—perhaps more indirect—way in which one symbiont may enhance the activity of another. It has long been known that the accumulation of the products of metabolism of a cell tend to inhibit the activity of that cell, and that if by any means we can destroy or remove the metabolite as it is formed, the cell concerned can go on working. Similarly with ferments, and even with enzymes, the accumulation of the products gradually inhibits the action, as Tammann showed in the case of amygdalin and emulsin, and Brown and Morris and Lea in the case of starch and diastase, to mention two illustrations only.

Now suppose we have two organisms, A and B, living in symbiosis, and suppose that A is capable of hydrolysing starch by the excretion of diastase, while B removes the product of hydrolysis, by fermenting the sugar as fast as it is formed; in this case there is every reason to expect that A will complete its hydrolysing action to the utmost, not only because it is of advantage to A to be relieved of the inhibiting sugar, but because the diminution of the sugar reacts as a stimulus to the secretion of more enzyme.

There is yet another point to be considered. Katz, in 1898, published some results confirming in many points the discoveries of Wortmann, Brown and Morris, and others, that fungi, bacteria, embryos, and other enzyme secreting organisms, not only vary the extent and kind of enzyme secreted, but can be stimulated to vary the enzyme according to the quantity or quality of food materials at hand.

I think this line of enquiry may lead to results in the present connection, as it is obvious that the products of fermentation of an organism A must be favourable, or without effect, or deleterious to the action of another, B, in its immediate neighbourhood. Moreover, it is shown that a product which is, *per se*, devoid of either favourable or deleterious action, may acquire one or the other if the concentration increases.

Katz regards the action of sugars as not a purely chemical one, but as a physiological stimulus; and without pretending to understand the distinction in detail, we may admit the importance of the experimental facts, and not only seek for, but also hope for, more light.

Here, then, is a brief sketch of some of the salient features of symbiosis, and of some of the physiological factors concerned in the processes; and though it is far from exhaustive, it may serve our purpose to-day of starting a discussion, and of showing some lines along which further investigation is desirable.

SYMBIOTIC FERMENTATION: ITS CHEMICAL ASPECTS.*

By Professor HENRY E. ARMSTRONG, F.R.S.

1. It is open to question whether the establishment of symbiotic relationships involves more than a subdivision of labour—whether the associated organisms combine in carrying the chemical change through any one phase.

2. There is an absence of positive evidence tending to show that the one member of a pair of symbiotic organisms or agents does more than prepare the way for the other by effecting a change which the second is incapable of inducing, leaving it to the second to carry on changes in which the initiating organism plays no part. A rough parallel to the case here contemplated would be that afforded by the occurrence of lactic followed by butyric fermentation under the influence of distinct organisms. These are strictly independent and sequent phenomena, the one change apparently setting in only when the other is complete.

3. In symbiotic fermentation, however, the two sets of changes seem at least to run parallel.

4. It may be a function of the one organism to remove from the sphere of action, as it arises, a product which would tend either to inhibit the change by which it is formed or to promote its reversal.

5. Or the one organism may produce a change which, although minute, is sufficient to place the companion organism under the most favourable conditions. For example, a minute proportion of acid favours the hydrolysis of cane-sugar by invertase. Hence it may be supposed that in a neutral or faintly alkaline solution yeast would ferment sugar only slowly, if at all, whilst if associated with an organism capable of producing, say, a minute proportion of lactic acid it would act rapidly. A case apparently of symbiosis, which possibly comes within this definition, is that referred to by Marshall Ward as studied by Van Senus.

6. Or, again, the one organism may become associated with the hydrolyte, and thus shield or mask a particular "centre" in it, thereby making it possible for the second

* Read before the British Association (Sections B and K), Dover Meeting, 1899.

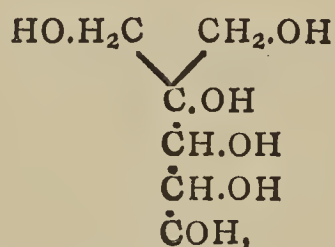
organism to actively affect the molecules at other centres. This case corresponds to the removal of a ward from a lock, and the consequent possibility of using a simpler key. What is in some cases a more nearly exact parallel is afforded by the production of glycuronic acid by the oxidation of the compound of glucose with chloral: in glucose, the COH centre is super-attractive to most oxidising agents, but when this centre is masked the attack is transferred to the opposite CH₂(OH) group.

7. Another case is considered subsequently (§ ii.).

8. Fermentation is certainly at bottom a process of *hydrocatalysis*, and it can scarcely be doubted that the function of the enzyme is to introduce water into the circuit of change—in fact, to establish a circuit in which hydrolytic changes can occur, although not of the ordinary kind, but reductive on the one hand and oxidative on the other.

9. Hence we may speak of the substance fermented as the *hydrolyte*, of the ferment as the *hydrolyst*, and of the products of hydrolysis as the *hydroschists*.

10. It is more than probable that the products ordinarily obtained are but end products of a series of changes, and that only some of these are enzymic, whilst others occur, as it were, naturally, and are partly analytic and partly synthetic in character. Thus, in the formation of the inactive amyl alcohol in fusel oil, it may be supposed that glucose is resolved by *fermentation* into a mixture of glyceraldehyde and glyceroketose, which spontaneously interact forming a new hexose,—



and that this in turn becomes *fermented* to isobutyl-carbinol, &c. It is not even known whether fusel oil is a product of fermentation by pure yeast; still less, therefore, can it be decided whether the two successive fermentations here contemplated are the acts of one organism, or of organisms which are in any sense symbiotic. But it seems almost certain that one and the same organism can produce a variety of changes.

11. It is conceivable that two symbiotic organisms may so act that the one produces a substance A, the other a substance B, and that these products interact, forming a third substance; and that the two organisms attack either one and the same substance, or different substances. In such a case the fermentation would be different from that produced by either organism singly. Such would be a case of truest symbiosis.

12. The conversion of lactic into butyric acid, of glycerol into butanol, and the formation of fat are certainly cases of fermentations in which synthetic changes occur, and it may well be apart from enzymic action.

13. There is little doubt that the importance of the part played by synthetic changes in fermentations, especially in the case of nitrogenous compounds, is at present far from being appreciated.

14. But however many steps may be involved in some fermentations, at least the attack on several centres must be simultaneous, and must occur in one and the same circuit, as the change involves expenditure of energy at some centres, and this must be supplied from those others at which energy is developed. A complex carbohydrate molecule undergoing fermentation may, in fact, be compared with a series of voltaic cells of unequal electromotive force in series. It is difficult in any other way to account for the re-resolution of a single molecule into so many others, such as occurs, for example, in ordinary alcoholic fermentation.

15. Such simultaneous attack is possible, probably be-

cause the enzyme is so constituted that it can attach itself at several points along the chain; the hydrolyte, in fact, is comparable with a complex lock, the hydrolyst with a complex key. It is possible thus to picture contact as being established between several more or less distant centres in a complex molecule, and a "ripple of change" as pervading the system in consequence. Enzymes with restricted powers, such as invertase and diastase, probably can attach themselves only to a single centre, and their action is directly and simply hydrolytic.

16. In some cases, such as the formation of fat, it would seem necessary to suppose that several molecules may become associated together through the agency of the hydrolyst, so that reductive processes may go on almost entirely in the one set; whilst in another corresponding oxidative processes take place, which furnish the energy required to effect the reduction. On the other hand, it is conceivable that oxygen directly intervenes in the formation of fat, and that the process is not merely one of hydrocatalysis.

17. That no very complex mechanism is needed to produce effects such as are believed to be involved in fermentations, follows from the fact that dextrose, for example, may be resolved into lactic acid by digestion with alkali and levulose into levulinic acid, CH₃.CO.CH₂.CH₂.COOH, by heating it with an acid, the latter being an especially remarkable case.

18. If the phenomena are as suggested, it does not seem probable that true symbiotic fermentation is likely to occur as a consequence of the simultaneous attack of a single molecule by several organisms; rather is it probable that associated molecules undergo change under the influence of a single organism or agent which determines their association. And hitherto apparently no case has been met with in which a substance has been observed to give way to a pair of organisms, neither of which can attack it singly.

19. The assimilation of nitrogen by plants, which is believed to take place in the symbiotic growths found on the roots of the Leguminosæ, is a phenomenon of which at present no explanation can be given, as this element cannot enter into combination with either hydrogen or oxygen unassisted; its absorption must take place in a circuit in which changes occur from which the necessary energy may be derived. As hydrogen is liberated in many fermentations, it appears not improbable that nitrogen may be brought into circuit by acting as a hydrogen depolariser; one function of the nodule may be to supply carbohydrate, which is fermented by the bacteroid in circuit with the nitrogen.

20. Symbiosis, as distinguished from parasitism, involves the conception not only of the concurrent existence of organisms, but of their useful concurrency; indeed, any other form of symbiosis is difficult to imagine, and *antisymbiosis* is a contradiction in terms. It is desirable that we should remain satisfied with the term until our knowledge of the actual character of the changes involved in ordinary as well as in symbiotic fermentations is far greater than is now the case; at present it is impossible to draw valid distinctions.

NOTE.—The explanation of fermentation adopted in this note is given in my Address to the Chemical Society in 1895 (*Trans.*, p. 1136). Green, in his recent work on Enzymes, speaks of Baeyer having put forward, in 1870, the hypothesis that fermentation is due to electric hydrolysis. This is incorrect. Baeyer's paper is entitled "Ueber die Wasserentziehung und ihre Bedeutung für das Pflanzenleben," &c. He makes no reference whatever to the manner in which water might be withdrawn, but merely shows that the withdrawal of water and the subsequent addition of its elements in a different order would produce effects such as are observed in fermentations.

CONDENSATION OF GLYCOLLIC ALDEHYDE.*

By HENRY J. HORSTMAN FENTON, M.A., F.R.S.,
and
HENRY JACKSON, B.A., B.Sc.

It has been pointed out by one of the authors in previous communications that tartaric acid when oxidised in presence of a small quantity of ferrous iron, gives rise to di-oxy-maleic acid, $C_4H_4O_6$; and that this acid readily decomposes in aqueous solution, giving glycollic aldehyde, $C_2H_4O_2$. This aldehyde has recently been isolated by the present authors in a crystalline state (*J. C. S. Trans.*, 1899, p. 575). It was further shown (Fenton, *Ibid.*, 1897, p. 375) that glycollic aldehyde, when heated to $100-105^\circ$ under reduced pressure, undergoes polymerisation, giving rise to a true hexose, $C_6H_{12}O_6$. The condensation effected in this way is not complete, and the resulting product has to be purified from the unaltered glycollic aldehyde by treatment with absolute alcohol; the yield of the sugar is consequently small, so that further study of its nature was extremely difficult.

The authors have therefore sought to modify the method of production with a view to increasing the yield, and have studied the results of effecting the condensation (1) at higher temperatures; (2) under the influence of alkalis.

If the aldehyde be heated to about $130-140^\circ$ for a short time a substance is obtained which dissolves easily in water, but is precipitated as a brownish white powder on addition of alcohol; whereas at a temperature of about $160-170^\circ$ a brown spongy substance is formed, which is nearly insoluble in boiling water, and on analysis its composition is found to be approximately $C_6H_{10}O_5$.

When an aqueous solution of the aldehyde is mixed with a dilute (1 per cent) solution of caustic soda, it begins to turn brown almost immediately. After standing for about twenty-four hours at the ordinary temperature (about 15°) the mixture no longer reduces Fehling's solution in the cold, nor answers Schiff's aldehyde reaction with magenta. The solution now gives with phenylhydrazin a precipitate consisting of clusters of bright yellow needles, which melt at 158° and have the composition of a hexosazone, $C_{18}H_{22}N_4O_4$. The pure osazone is very soluble in ethylacetate, sparingly soluble in ether, benzene, and boiling water. The crystalline form, melting-point, and behaviour towards solvents appear definitely to establish its identity with β -acrosazone, which was obtained by Fischer and Tafel from the condensation-product of "glycerose" by alkalis.

When calcium hydroxide is employed in place of caustic soda, an exactly similar result is obtained. After removing the calcium from the solution by exact precipitation with oxalic acid and evaporating to small bulk at 40° under diminished pressure, it was dissolved in alcohol, filtered, and then precipitated with ether. The sugar was thus obtained in the form of white flocks which aggregate to a pasty solid on standing in a vacuum.

The properties and configuration of β -acrose have not hitherto been studied, owing to the fact that it could not be obtained in quantity unaccompanied by other sugars; the authors hope, however, by the present method of preparation to obtain the sugar in quantity sufficient for a more complete study.

The formation of a true hexose, and a substance resembling starch and cellulose, from glycollic aldehyde, is of especial interest from its bearing on carbohydrate formation in plants. The remarkable part which a small quantity of ferrous iron plays as a carrier of atmospheric oxygen in presence of direct sunlight has already been pointed out (Fenton, *Brit. Assoc. Report*, 1895; Fenton and Jackson, *Trans. Chem. Soc.*, 1899, 1): in the absence of any of these three conditions, the oxidation does not take place. In plant metabolism these conditions coexist; this reaction may not only throw light upon the function

of small quantities of iron existing in chlorophyll, but may explain the conversion of tartaric acid, which is so common in unripe fruits, to the sugars of the mature fruit.

THE ACTION OF IODIDE OF POTASSIUM IN SOLUTION ON MERCUROUS IODIDE.

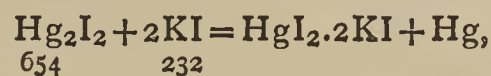
By MAURICE FRANCOIS.

I HAVE already shown that mercurous iodide is easily decomposed into mercury and dissolved mercuric iodide under the influence of a certain number of liquids, and that these reversible decompositions obey the laws of the dissociation of salts by water. To conclude this subject I will describe, as obeying the same laws, the action of solutions of iodide of potassium on mercurous iodide.

We know that iodide of potassium decomposes mercurous iodide into mercury which is deposited, and mercuric iodide which goes into solution. The following are the facts which I observed when operating at a constant temperature of 20° , and acting on mercurous iodide with a normal solution of pure iodide of potassium (166 grms. per litre).

Complete Decomposition.—The decomposition is complete when the iodide of potassium is used in large quantity—for example, if we agitate 2 grms. of mercuric iodide with 20 c.c. of the normal solution of iodide of potassium. The insoluble portion is formed entirely of small globules of mercury.

Incomplete Decomposition.—If the quantity of mercurous iodide is more considerable, a portion only is decomposed. The insoluble portion is a greenish-yellow powder, formed of a mixture of mercurous iodide and finely divided mercury. This is what happens when, for instance, we agitate 20 c.c. of the normal solution of iodide of potassium with 6.54 grms. of mercurous iodide. The actual proportions used are those corresponding to the following equation:—



by which is represented generally the action of iodide of potassium on mercurous iodide. The action is thus limited. Whatever may be the proportions used, when the decomposition stops and equilibrium is reached, 100 grms. of the supernatant liquid contains 11.9 grms. of mercuric iodide in solution at a temperature of 20° .

Inverse Action.—If we saturate a certain quantity of the normal solution of iodide of potassium at 20° with mercuric iodide, this solution—when placed in contact with metallic mercury—attacks it in the cold and mercurous iodide is formed in abundance. But this inverse formation of mercurous iodide stops of itself when a large proportion of mercurous iodide is present in the solution.

For the temperature of 20° we find that, at the moment when equilibrium is established, 100 grms. of the liquid contains 11.9 grms. of mercurous iodide in solution—a figure already found in the experiment on decomposition.

We have used the normal solution of iodide of potassium, but it is evident that these facts will equally apply to solutions of different concentration. Nessler's reagent attacks metallic mercury very energetically, giving mercurous iodide. The preceding determinations were made in the following manner:—For the limited decomposition we left 200 c.c. of the normal solution of iodide of potassium and 65.4 grms. of mercurous iodide in contact for twenty-four hours, in an oven kept at 20° , with constant stirring. At the end of this time we take 5 c.c. of the clear supernatant liquid and determine its weight, and estimate the mercury and the iodine by electrolysis.

To make the same determination in the inverse action we left 100 c.c. of the normal solution of iodide of potassium saturated with mercuric iodide and 200 grms.

*Read before the British Association (Section B), Dover Meeting, 1899.

of mercury in contact for twenty-four hours, with frequent stirring. At the end of this time we took, as above, 5 c.c. of the clear liquid for the estimation, after weighing, of the mercury and the iodine.—*Journ. de Pharm. et de Chim.*, Series 6, vol. x., No. 1,

VOLUMETRIC ESTIMATION OF PHOSPHORIC ACID IN PHOSPHATES.

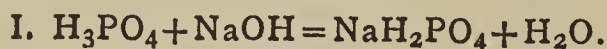
By Dr. SIGISMUND LITTMANN.

THE numerous experiments that have been made of late years for the purpose of obtaining a rapid and practical method for the estimation of phosphoric acid in phosphates, shows very clearly that all the usual methods employed, even those using citrate, are too long and inconvenient.

In what follows I propose to explain a new method, very easy of execution, of which the results are rigorously exact, and which fulfils all the requirements of practical chemists, as will be seen from the subjoined analyses.

The manner in which orthophosphoric acid behaves with alkalis and various indicators is known, but perhaps not sufficiently appreciated. I may mention that, in my opinion, the best indicators are methyl-orange and phenolphthalein.

The salts of orthophosphoric acid give alkaline and not neutral reactions with these bodies; the reactions of the monohydrodimetallic phosphates, and of the dihydromonometallic phosphates with methyl-orange are alkaline, and with phenolphthalein they are acid, while with the free acid, H_3PO_4 , the reactions are acid with both bodies. The usual method for determining the acidity of phosphoric acid is founded on this manner of behaving. Although well known it is as well to draw attention to the successive saturation by means of equations. Starting from free H_3PO_4 we obtain, after having added methyl-orange until the yellow colouration titrates with caustic soda, monophosphate of soda.



After the addition of phenolphthalein until a red colouration appears, on adding NaOH we obtain diphosphate of sodium—



the red colouration taking place at the moment of the formation of the normal triphosphate,—



In this manner orthophosphoric acid may be easily determined in the presence of other acids, provided that the acids which may be present are modified by the first saturation (I.); H_3PO_4 is only transformed into NaH_2PO_4 , which is estimated after the second saturation, by means of phenolphthalein.

The objection which has been made to this method—above all, when using one-tenth normal soda—that the reading is not sufficiently sharp considering that the transformation of NaH_2PO_4 into Na_2HPO_4 corresponds to the state called “amphotere,” is not altogether unfounded, but the errors arising from this imperfection may be reduced to a minimum, as is shown by the following analyses.

A certain number of mixtures of HCl , H_2SO_4 , HNO_3 , and H_3PO_4 in varying quantities (the H_3PO_4 was obtained from a solution of P_2O_5 boiled for some time with HNO_3 , until the metaphosphoric acid is completely transformed) were titrated with one-tenth normal soda; the phosphoric acid in each mixture was also determined gravimetrically with molybdate of ammonia.

P_2O_5 per cent.		
Gravimetric results.	By titration.	Difference.
2.30	2.26	0.04
3.84	3.80	0.04
5.78	5.72	0.06
11.33	11.08	0.25
11.47	11.39	0.08
14.49	14.31	0.18
21.87	21.78	0.09

From the results obtained by titration it appears that a proportion of 0.016 per cent was obtained.

Our object is now to make use of this behaviour of orthophosphoric acid for phosphates. The titration with caustic soda gives useless results, as was foreseen in view of the diversity of the bases with which the H_3PO_4 is united and their precipitation by the alkali. It became necessary to transform the monophosphate of calcium and the other phosphates (Mg, Al, Fe) into phosphates of the alkali, and prevent the precipitation of the bases.

R. J. Thomson's method (precipitation by oxalate of soda or ammonium) represents an experiment of this character.

This method, which will not do with phosphates containing iron, is very little used in practice.

For effecting this transformation I use an alkaline citrate; in the course of my experiments, I found that citrate of sodium gave better results than the corresponding salts of potash and ammonium.

It is essential for the citrate to be absolutely neutral. As to its preparation, it is as well to follow the subjoined method:—A pure solution of NaOH (30 grms. of NaOH in 120 c.c. of water) is neutralised, after having added phenolphthalein, with concentrated citric acid, then after twenty-four hours the liquid is filtered so as to separate any precipitate which may have formed; if necessary, it is neutralised a second time and then diluted to 120 c.c.

This solution will keep for a considerable time in well stoppered bottles; it is always as well to test its neutrality before using it. Further, the one-tenth normal solution of NaOH should not contain carbonic acid, and should not be contaminated with either $\text{Ca}(\text{OH})_2$ or $\text{Ba}(\text{OH})_2$. For the purpose of analysis 10 grms. of phosphate are dissolved in 400 c.c. of water in a flask of 500 c.c. capacity. After having shaken for about half an hour, the flask is filled up to the mark; filter, and use 50 c.c., equivalent to 1 gm., for the titration; add methyl-orange, titrate until there is a distinct yellow colouration, and note the quantity of one-tenth normal NaOH which has been used.

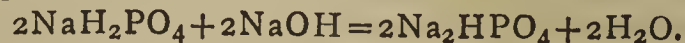
Besides the $\text{CaH}_4(\text{PO}_4)_2$, we have still NaH_2PO_4 produced from the H_3PO_4 . The first body is transformed into NaH_2PO_4 by the addition of 10 c.c. of the citrate solution, $\text{Na}_2\text{C}_6\text{H}_6\text{O}_7 + \text{CaH}(\text{PO}_4)_2 = \text{CaC}_6\text{H}_6\text{O}_7 + 2\text{NaH}_2\text{PO}_4$.

The solution is generally of a greenish colour, owing to the presence of citrate of iron; this considerably facilitates the observation of the change of colour after the addition of phenolphthalein. The titration should be continued to a red colouration; this operation requires very great care.

The titration is finished slightly before the faint red colouration which is caused by the Na_3PO_4 appears. After a few trials we can easily detect the end of the reaction by adding soda until the red colouration is distinct (working on a sheet of white paper) and titrating back with one-tenth normal H_2SO_4 until the colouration disappears.

During this second saturation the solution remains clear; this is a very great advantage over other analogous methods.

The neutralisation may be represented by the following equation:—



We obtain the content per cent of P_2O_5 by multiplying the cubic centimetres of soda used in the operation by 0.71.

Gravimetric results.		By titration.		Difference. P ₂ O ₅ . Per cent.
Mg ₃ P ₂ O ₇ .	P ₂ O ₅ .	One-tenth normal NaOH.	P ₂ O ₅ .	
	Per cent.	C.c.	Per cent.	
Florida Phosphate.				
0.2757	17.65	24.7	17.54	- 0.11
0.2722	17.42	24.8	17.61	+ 0.19
0.2844	18.20	25.7	18.24	+ 0.44
0.2706	17.32	24.9	17.68	+ 0.36
0.2809	17.98	25.3	17.96	- 0.02
0.2672	17.10	24.5	17.39	+ 0.29
0.2695	17.25	24.3	17.25	0.00
0.2608	16.69	23.8	16.89	+ 0.20
0.2813	18.00	25.6	18.18	+ 0.18
0.2766	17.71	25.0	17.75	+ 0.04
0.2800	17.92	24.9	17.70	- 0.22
0.2772	17.74	25.0	17.75	+ 0.01
0.2826	18.08	25.6	18.17	+ 0.09
0.2768	17.72	24.8	17.61	- 0.11
0.2758	17.65	25.0	17.75	+ 0.10
Bone-ash.				
0.2965	18.98	26.4	18.74	- 0.24
0.2669	17.08	24.3	17.23	+ 0.15
0.2667	17.07	24.1	17.11	+ 0.04
0.2983	19.09	26.6	18.99	- 0.20
0.2728	17.39	24.4	17.32	- 0.07
0.2834	18.14	25.4	18.03	- 0.11
0.3005	19.23	27.3	19.38	+ 0.15
0.2820	18.05	25.2	17.89	- 0.16
0.3008	19.25	27.3	19.38	+ 0.13
0.2518	16.11	23.0	16.33	+ 0.22
Algerian Phosphates.				
0.2505	16.03	22.7	16.11	+ 0.08
0.2610	16.70	23.6	16.76	+ 0.06
0.2442	15.63	21.8	15.48	+ 0.15
0.2605	16.67	23.5	16.68	+ 0.01
0.2472	15.82	22.4	15.90	+ 0.08
0.2323	14.87	20.8	14.78	- 0.09
0.2520	16.32	23.5	16.68	+ 0.36
0.2405	15.39	21.8	15.47	+ 0.08
0.2580	16.51	23.5	16.68	+ 0.17
0.2252	14.41	20.3	14.41	0.00
0.2505	16.03	22.6	16.05	+ 0.02
0.2453	15.70	22.7	16.18	+ 0.41
0.2452	15.69	22.5	15.97	+ 0.28
0.2497	15.98	22.4	15.90	- 0.08
0.2460	15.74	22.2	15.76	+ 0.02
Special Manure.				
0.1019	6.52	9.1	6.46	- 0.06
0.1606	10.28	14.6	10.36	+ 0.08
0.2472	15.82	22.1	15.70	- 0.12
0.2353	15.06	20.7	14.77	- 0.29
0.2100	13.44	19.0	13.49	+ 0.05
0.2062	13.19	18.4	13.06	- 0.13
0.1426	9.12	12.7	9.02	- 0.10
0.1876	11.98	17.1	12.14	+ 0.16
0.1540	9.85	13.8	9.80	- 0.05
0.1224	7.86	11.1	7.99	+ 0.13

There are some phosphates—especially those which contain much iron or alumina—with which the change of colour of the methyl-orange from red to yellow is not sufficiently distinct, the salts of iron and alumina themselves having an acid reaction.

The change becomes more distinct by diluting the 50 c.c. five times; for such a titration it is necessary to then take 50 c.c. of that solution, add to it 10 c.c. of the solution of citrate without previously diluting, add the phenolphthalein, and complete the titration. The quantity of soda used in the first place is deducted.

It is, as a rule, of advantage to proceed in this manner,

the yellow colouration of the methyl-orange being thus eliminated. It is evident that this method enables us to estimate the total phosphoric acid, and not only the phosphates soluble in water; however, in the presence of large quantities of acids the work becomes less easy and the results not so correct. The meta- and pyrophosphoric acids cannot be estimated in this manner.

I have attempted to use a few other indicators, such as litmus, cochineal, tropeoline, curcuma, &c., but without success.

Each analysis—comprising half an hour for extraction and shaking up the solution—lasts only three-quarters of an hour; the double titration, with the necessary calculations, hardly requires five minutes.

I have been using this method for about a year for the analysis of Florida and Algerian phosphates and bone-ashes, as well as for several special manures containing sulphates of potash and ammonium.

The comparative gravimetric method which I used was the citrate method; the one which I have just mentioned might, however, replace it. In some cases, where there were large differences (a maximum of 0.4 per cent), I used the molybdate method, with which I obtained results more in accord with those obtained by titration. The difference with regard to the gravimetric method (citrate) is about 0.13 per cent.

Its exactness and its easy manipulation cause me to believe that this process, in spite of the large number of methods already proposed, will be welcomed by those chemists whom it most concerns.—*Chemiker Zeitung*, xx., No. 68.

ANALYTICAL METHODS FOR DISTINGUISHING BETWEEN NITROGEN OF PROTEIDS AND NITROGEN OF SIMPLER AMIDES OR AMIDO-ACIDS.

By J. W. MALLET,
Professor of Chemistry, University of Virginia.
(Concluded from p. 171).

Behaviour with Cupric Hydroxide (Stutzer's Reagent).

THE formation of insoluble compounds of the proteids with cupric hydroxide, while leaving the simpler amides soluble in the presence of an excess of this reagent, has been extensively adopted as the means of separation, but experiments made in this way have not given the writer much confidence in the method as a general one. In some cases, working with a proteid alone, the copper compound underwent partial solution, a blue liquid being formed, although care had been taken to avoid the presence of free alkali. Possibly this result was due to incipient decomposition of the proteid material. As Stutzer himself has pointed out, peptones are very incompletely precipitated by cupric hydroxide. A further objection is to be found in the very slight solubility of the copper salts of some of the simpler amido-acids, especially leucin and glutamic acid; in a less degree the same statement applies to aspartic acid. Even at the temperature of boiling water the copper compounds of these substances are but very sparingly soluble, and if the liquid after digestion with cupric hydroxide be filtered cold,* the compounds in question will, if present, be almost certainly left on the filter along with the proteid material.

Relations to Alcohol as a Solvent.

It has been repeatedly proposed to use strong alcohol for the precipitation of the proteids, with a view to their quantitative determination, and this even in cases involving the simultaneous presence of some of the amidic com-

* As directed by the Association of Official Agricultural Chemists, Bulletin No. 46 of the U.S. Department of Agriculture, Division of Chemistry (1895), p. 25.

pounds under discussion, such as the flesh bases (See Watts's "Dictionary of Chemistry," revised edition, vol. iv., p. 330, and H. W. Wiley's "Principles and Practice of Agricultural Analysis," vol. iii., p. 453). But not only do the character and amount of the proteids so precipitated or left insoluble vary with the strength of the alcohol and the quantity of it used, but the further serious objection presents itself, that nearly all the simpler amides and amido acids are either insoluble in alcohol or so slightly soluble that it is practically impossible to wash them out satisfactorily from the precipitated or coagulated proteids. A method which is not properly applicable to such important substances as asparagin among vegetable food materials, and kreatin among those of animal origin, manifestly deserves but little consideration.

Behaviour with several New or Little-used Reagents.

A number of miscellaneous experiments were tried with reagents which have either been but occasionally applied to materials of the kind under examination, or have not been so applied at all, so far as published records show.

A weak solution of pure phenol (carbolic acid), trichloroacetic acid, formic aldehyde in aqueous solution, and hydrazoic acid (azoimide) were thus tried, but from none of these reagents were results obtained which furnished any ground for a general method of distinguishing the two classes of nitrogenous materials which were being studied.

Behaviour with Phospho-tungstic Acid.

This reagent, the discussion of which I have left to the last, has proved of much more value than any other I have tried, and its application under proper conditions affords, I believe, a fairly satisfactory practical solution of the question I have undertaken to examine. The use of phospho-tungstic acid for the precipitation in general of nitrogenous compounds, alkaloidal, amidic, and proteid, is, of course, well known and often practised; but some of the special facts on which may be founded its application to the purpose now under discussion are believed to be new, and the particular use made of these points of behaviour has not been before described. In connection with the experiments made with phospho-tungstic acid, the results obtainable from a parallel series of experiments with a strong solution of tannic acid were compared, one of these two reagents being found under special circumstances to replace the other with advantage.

The precipitant was employed not as a sodium or other salt, but as the phospho-duodeci-tungstic acid, crystallised in small cubes and dissolved in dilute hydrochloric acid, 25 grms. of real HCl to the litre. Solutions of 2 degrees of strength were prepared, the one containing 50 grms. of the solid reagent to the litre, the other 100 grms. In the experiments with tannic acid, solutions in like manner containing 50 and 100 grms., respectively, of a remarkably good sample of the reagent, dissolving readily to a perfectly clear liquid, were made use of.

It has been assumed by Stutzer and others that the proteid and allied substances are precipitated by phospho-tungstic acid, while the simpler amides and amido acids are not so precipitated. As qualifying this general assumption, it has been stated that some of the proteid derivatives, as the peptones* are incompletely precipitated, and on the other hand that the flesh bases, kreatin, kreatinin, &c., are fully precipitated. The reagent in question has been recommended as the means of separating and determining them (Koenig and Boemer, *Zeits. für Anal. Chemie*, xxxiv., 560, adopted in Prof. H. W. Wiley's "Principles and Practice of Agricultural Analysis," iii., 454).

*Dr. W. H. Halliburton, in the article 'Proteids' in Watts's "Dictionary of Chemistry," revised edition, vol. iv., p. 331. In Gamgee's "Text-book of Physiological Chemistry," vol. ii., p. 139, it is stated that peptones are precipitated by phospho-tungstic and phospho-molybdic acids, and that these two reagents furnish the means of separating them. A similar unqualified statement is to be found in the Appendix (by A. Sheridan Lea) to Michael Foster's "Text-book of Physiology," p. 45.

Account does not seem to have been taken hitherto of the fact that some of the precipitates formed by substances of amidic character with phospho-tungstic acid are to a small extent soluble in water, and that their solubility is much increased by rise of temperature.

Classification of Substances Examined.

It has been found that the various substances on which these experiments have been made fall into three classes as follows:—

(a). Those which, even in pretty strong solution, give no precipitate with phospho-tungstic acid.

(b). Those which are precipitated at any rate in strong solutions, the precipitate re-dissolving with more or less ease on heat being applied to the liquid or on treating the precipitate with hot water, and re-appearing on cooling.

(c). Those which are precipitated, the precipitate not being sensibly soluble and the supernatant liquid remaining clear on being heated along with the precipitate and subsequently cooled.

Under the first head fall glycocin, alanin, leucin, aspartic acid, asparagin, glutamic acid, tyrosin, and allantoin. In the case of alanin there was a very slight turbidity not increased by using a saturated solution, suggesting the probability of a trace of some impurity being present.

Under the second head were observed glutamin, a slight precipitate, the solution easily cleared by heating, the turbidity re-appearing on cooling; betaine in strong solution, a copious white precipitate, dissolving gradually on addition of more water and heating, the precipitate re-appearing on cooling; kreatin, strong precipitate, solution cleared by heating, becoming turbid again on cooling; kreatinin, large precipitate, disappearing on free addition of water and heating, reappearing on cooling; hypoxanthine, strong precipitate, cleared up on heating, re-appearing on cooling; and carnine, well-marked precipitate, cleared by moderate addition of water and heating, reappearing on cooling. Urea also, which is not likely to occur among food materials, but possibly needs to be considered in connection with undigested residue, gave a copious white precipitate of crystalline character, cleared by heating, and the precipitate forming anew on cooling. A peptone solution gave an abundant precipitate, becoming clotted by heating, and dissolving to a considerable extent, re-precipitating on cooling.

Under the third head were found egg albumen, fibrin, casein, legumin, globulin, vitellin, myosin, syntonin, hæmoglobin, albumose, gelatin, and chondrin. In nearly all these cases the precipitate formed was bulky, taking into account the strength of the solution used, and became clotted on heating, shrinking very considerably. In the case of myosin only (in 10 per cent sodium chloride solution) was there a very slight appearance of turbidity on cooling the solution which had been heated with the precipitate.

Use of Hot Water.

As it was evidently important to ascertain with some degree of definiteness how far the precipitates formed by amidic substances of the second of these classes would dissolve in hot water, quantitative experiments were made with those which seemed to be least soluble. In each case the precipitate formed by phospho-tungstic acid in the cold was filtered off, washed with cold water, and dried at ordinary temperature (15° to 20°) over sulphuric acid. Stutzer advises that the phospho-tungstic acid precipitates be washed with dilute sulphuric acid, and Wiley recommends for the same purpose a solution of the precipitates. Of the precipitate formed by betaine, 1 part dissolved in 71 parts of water at 98.2°; of that produced by kreatin,* 1 part dissolved in 107 of water at

* The phospho-tungstic acid precipitate, formed by kreatin, white at first, darkened notably on exposure to light, looking after a while like silver chloride which had been in like manner exposed. The experiment on solubility was made with a sample which had been screened from light and was unaltered.

98.1°; of that produced by kreatinin, 1 part dissolved in 222 of water at 97.9°; of that produced by hypoxanthin, 1 part dissolved in 98 of water at 97.6°; and of that produced by carnin, 1 part required for solution 132 of water at 98.4°.

By the use of phospho-tungstic acid as a precipitant, therefore, followed by washing of the precipitate with hot water, it seems possible to effect a separation of all the simpler amidic substances from all the proteids and proteid-like bodies, except only the peptones. As regards this last group it is stated unreservedly by A. S. Lea ('The Chemical Basis of the Animal Body,' an Appendix to M. Foster's "Text-book of Physiology," 1893, p. 45), A. Gamgee ("A Text-book of the Physiological Chemistry of the Animal Body," 1893, ii., 139), and W. D. Halliburton (Watts's "Dictionary of Chemistry," revised edition, 1894, iv., 331), that the peptones are precipitated by tannic acid. The last-named writer says "completely precipitated." In one or two of the writer's own experiments, using tannic acid, an abundant precipitate was formed. This became clotted on heating, and the clear supernatant liquid showed some little return of turbidity on cooling. The writer is inclined, however, to attribute this apparent partial re-solution of the precipitate merely to the presence of a little of a proteose formed in the earlier stages of digestion and not afterwards completely removed. Assuming this view to be correct, tannic acid furnishes the reagent needed to dispose of the one case unprovided for by phospho-tungstic acid.

Details of the Method with Phospho-tungstic Acid.

The method proposed is as given in the following paragraphs. It is stated, for the sake of simplicity, first, as applicable to meat, raw or cooked. The variations required in the examination of other classes of food materials are reserved for notice afterwards.

A carefully selected and accurately weighed sample is to be ground in a glazed porcelain mortar with as much sharp-edged siliceous sand, previously heated to redness with free exposure to air, or with as much hard glass in small sharp splinters similarly ignited, as shall suffice to thoroughly subdivide the tissue and reduce it to the condition of a smooth pulp. Of this pulp, very carefully mixed, so as to insure uniformity, two aliquot parts are to be taken. In one the total nitrogen is to be determined by the well-known Kjeldahl process with the addition of potassium sulphate, as recommended by Gunning, using a rather large proportion of sulphuric acid, so that no previous drying of the sample is needed. The other part is to be digested with cold water, filtered on a nitrogen-free filter,* and the residue washed on the filter with water at the same low temperature as long as it gives up soluble matter in sensible amount. Cold water is used to avoid action on and extraction of the gelatinoids. Creatinin is quite easily dissolved, as is also sarcosine; creatin with a very fair degree of ease. Xanthin, hypoxanthin, and carnin are less soluble.†

The filtrate is then to be slightly acidified with acetic acid, heated to about 90° C., and again filtered from any coagulum produced. A little more sand or pulverised glass may with advantage be stirred in before bringing it on to the filter the second time.

To this second filtrate is to be added an acidified solution of phospho-tungstic acid as long as a precipitate continues to form, avoiding any very large excess of the reagent solution. With a moderate amount of sand or pulverised glass added, to prevent the formation of a dense clot, the liquid and precipitate are to be heated to about 90° C., filtered, and the precipitate washed thoroughly on the filter with water at about the same temperature. This third filtration may be carried out on the same filter

already used for the second, but as a general rule it will be found better to use a new filter, thus avoiding possible delay due to partial drying of the previously used one and subsequent clogging of its pores.

Assuming now that nitrogen is present in the sample under examination only in the two forms of proteids and simpler amidic compounds, the three (or two) filters used and their contents are to be submitted to the Gunning-Kjeldahl process for the determination of proteid nitrogen. By subtraction of this from the total nitrogen previously determined the amount of this element present in the simpler amidic compounds will be obtained.

In cases involving the presence of ammonia or its salts, nitrates, or alkaloids, the nitrogen occurring in these forms must, of course, also be deducted from the total nitrogen before recording the residue as nitrogen of the simpler amides and amido-acids. In like manner a separation of lecithin, when present, may be effected by the use of ether as a solvent,* a determination of phosphorus made the basis of a calculation of lecithin nitrogen, and this in turn extracted from the total nitrogen found.

When peptones are present, these are to be precipitated by tannic acid from the solution which has been acidified with acetic acid and heated. After this has completely cooled down, and before adding phospho-tungstic acid, the filter on which the tannic acid precipitate is collected and washed with cold water is, with its contents, to be submitted to the modified Kjeldahl process, and the nitrogen obtained counted as part of the proteid nitrogen.

The several filters and precipitates from which the proteid nitrogen is obtained may either be treated separately by the Kjeldahl process or, preferably, may all be brought together and submitted to this process in a single operation. If the latter course be pursued, it will be well to introduce each filter with its contents as soon as washed into the strong sulphuric acid, so as to avoid any possible decomposition and loss of nitrogen as ammonia until all the filters have been brought together and the moist combustion process can be proceeded with.

When proteoses are present it may be well to make a check determination of their amount by saturation of the aqueous solution, after acidification with acetic acid, heating, and subsequent cooling, with zinc sulphate (as suggested by Boemer, *Zeit. Anal. Chemie*, 1895, xxxiv., 562), and determining nitrogen in the precipitate so formed by means of the Kjeldahl process.

When gelatinoids are present, as may be the case with soups, stews, and meat extracts, hot water may be used at once for solution or washing the original material, and this with the advantage of facilitating the extraction of the less soluble simpler amides and amido-acids. These are, as a rule, more easily dissolved in the presence of a little free acid; hence acidification at an early stage of the treatment is advantageous. In a case in which tyrosin might be present, as in some vegetable materials, and possibly among unabsorbed residua of food, the use of hot water and the presence of free acid would greatly increase the solubility of this substance.

In food of vegetable origin where much starch is present it will be better to avoid the use of hot water at first, so that the solution may not be loaded with viscid material, rendering filtration difficult.

In all cases in which the food material to be examined is already fluid from the presence of water—as, for instance, soup, milk, and the like—filtration will, of course, at once be resorted to, being almost always much facilitated by the addition of sand or pulverised glass, and only such further quantity of water will be used as is required for washing the undissolved matter left upon the filter.

In the presence of fat in large quantity, it may be well first to remove this, or most of it, by extraction with ether. The simpler amidic substances are, as a rule, insoluble in ether, but by way of precaution the ethereal solution of

* The ease with which filtration may be effected is much increased by the presence of the sand or crushed glass.

† Hypoxanthine, 1 part in 300 of water. The solubility of carnine does not seem to have been recorded till now. The writer has found it to be 1 part in 312 of water at 15.3° C.

* Extraction with the ether alone will remove only a portion of the lecithins. A mixture of ether and alcohol should follow the ether in order to secure a complete extraction.

fats might be shaken up two or three times with acidified water, and the watery fluid evaporated and tested for nitrogen.

In regard to the method of reporting results, the most important point is the separate statement of the amount of nitrogen present in the form of proteids and their more closely related congeners and in the form of the simpler amides and amido acids. But in attempting to calculate from the nitrogen found under these heads the actual amount of the proximate nitrogenous constituents of the food material examined, the question arises—What factor should be used by which to multiply the nitrogen found in each case?

Factors for Calculation of Total Nitrogen.

The error noticed by Professor Wiley ("Principles and Practice of Agricultural Analysis," 1897, iii., 551) as involved in the multiplication of the total nitrogen of a sample of meat by 6.25, and the assumption that the product represents the true quantity of nitrogenous matter, is not restricted to the use of the same factor for the proteids and flesh bases. While the multiplier should be a much smaller one for the latter, it also confounds under a single head these two classes of material, unquestionably possessing very different nutritive values.

It is evident that for each substance examined, or at any rate for each class of generally similar food materials, there should be made a qualitative investigation of the simpler amidic constituents present, and if possible a roughly approximate estimate of the proportions in which they severally occur; also it is clear that the factor to be used in calculating the nitrogenous constituents to be reported under each analysis should be decided by such preliminary investigation. In the light of present knowledge the writer is inclined to suggest the following numbers:—

For proteids and allied substances, multiply nitrogen found by 6.25, as usual at present.

For flesh bases and simpler amides of animal origin in food materials, multiply by 3.05.

For simpler amides and amido-acids of vegetable origin in food materials, multiply by 5.15.

For mixed amidic constituents of unabsorbed solid residua in digestion experiments, multiply by 9.45.

As a matter of general practice, in all statements of the results of nutrition experiments the rule should be invariably observed to give the actual amounts of nitrogen obtained by analysis, whatever calculated conclusions be afterwards deduced therefrom; so that, with further knowledge of the nature of the proximate nitrogenous constituents present, the factor used in calculation may be changed, if such change seems to be called for, while the original experimental work still retains its value.

In concluding this report, the writer wishes to express the hope that the method suggested, which seems to carry with it some improvement upon present practice and in a fairly simple and easily applied form, may be tried with yet other amides and proteids than those experimented on by him, and that any special difficulties which may be encountered with particular articles of food may be investigated. Especially is it desirable that the variations be studied which may prove to be necessary in dealing with vegetable instead of animal materials. The latter have been chiefly kept in view, in accordance with the instructions of the letter of authorisation under which this investigation has been conducted.

On the Isomeric Benzoylketoximes.—J. Schmidt.—The author has prepared a liquid isomer of benzoylketoxime, by reacting with chloride of benzoyl on the soda derivative of acetoxime. The reaction should be carried out in the cold; sodium is added to acetoxime and ether; when all the sodium has changed into a white crystalline mass, it is filtered and washed with ether; pure chloride of benzoyl and anhydrous ether are then added in the cold. When the reaction is finished, filter and evaporate *in vacuo*. The solid isomer is gradually deposited, and can be easily removed.—*Berichte*.

THE SOUTHAMPTON BACTERIAL SYSTEM AT SOUTHWOLD.

MR. FREDK. BALL, Civil Engineer, Borough Surveyor of Southwold, reports that, in consequence of the Sewage Works at the time of his succession to the office of Borough Surveyor of Southwold being inadequate, Mr. Candy, of the International Purification Syndicate, was instructed to submit a scheme for the Bacterial treatment of the sewage upon the Polarite Oxidising system, in order to test—which it was decided to utilise—one of the three existing precipitation tanks. The Southwold sewage, it should be mentioned, is excessively foul and concentrated, owing to the small consumption of water.

The tank was divided into two compartments, to form an anaërobic sludge digesting bed and an aërobic or polarite oxidising bed.

Crude sewage is admitted to the detritus chamber wherein the grit is deposited, and paper and floating solids are arrested until sufficiently disintegrated to be carried into the anaërobic bed through slotted wooden troughs laid below the surface of the anaërobic bed, being thus evenly distributed.

This bed consists of large cobble stones from the beach laid to a depth of about 4 feet. On the top of the cobbles the slotted wooden troughs are laid, and the whole covered over with gravel so that anaërobic conditions are obtained.

The liquid sewage passes equally downwards through the bed, and is collected into a brick channel with iron outlet pipes, fixed in the top and rising above the level of the inlet troughs, but not up to the level of the top fine gravel, which thus presents a clean and pleasing surface, expensive arching over being altogether avoided.

These pipes discharge into an open trough which feeds the self-propelled revolving sprinklers and aërotors (Candy's patent) that deliver the anaërobic effluent on to the rapid oxidising polarite bed, which effects the final purification by oxidising the soluble impurities and nitrifying the ammonia.

This system of working Bacteria beds constitutes a marked advance in efficiency and economy over the contact method of filling, stagnating, drawing off, and resting.

The quantity of sewage treated is 500 to 600 gallons per square yard of filtering area per twenty-four hours; the aërobic beds are only 2 feet thick, on account of want of fall.

The sewage of Southwold, as before stated, is very strong, as indicated by analysis, but the effluent is also shown by analysis to be an excellent one.

The result of a series of analyses of Southwold polarite oxidising Bacteria effluents shows from 92 to 98 per cent of purification, with average nitrates 3.36 grms. per gallon.

Mr. Ball reports that, in his opinion, the shallowness of the bed combined with the high speed of filtration and the foulness of the sewage render the results obtained satisfactory in the highest degree, and constitute a great achievement in economical sewage purification.

The system has been in operation since the 16th of April last, and there are no signs of sludge or choking of the bacteria beds. The chief object in adopting this bacterial system was to obtain the abolition of sludge. So successful has it been that arrangements are being made to treat the whole of the sewage by this system.

Apart from the chemical evidence of the purity of the effluent, one has but to view the old and the new systems, working side by side, to realise the advantages of the latter.

In the old system there are large tanks full of sewage covered with foul-smelling septic scum, and tons of sludge to be disposed of. In the new system no sewage is

visible but the comparatively clear liquid periodically discharged through the revolving sprinklers.

In the place of the sewage scum there is the clean surface of the polarite oxidising bed, and there is also the untold advantage of the absence of sludge.

CORRESPONDENCE.

SUPERCOOLING OF PHOSPHORUS.

To the Editor of the Chemical News.

SIR,—The supercooling of water is a well-known phenomenon, but it is somewhat difficult to show as a lecture experiment, as it requires a good deal of preparation. The supercooling of liquid phosphorus, on the other hand, is exceedingly simple to demonstrate. If a piece of phosphorus be melted under a strong solution of caustic soda or potash, as in the preparation of phosphoretted hydrogen, it will remain liquid apparently for an indefinite time; at any rate, I have kept some four days in that condition. Its temperature can be taken roughly by immersing a thermometer bulb in it, and it will bear moderate shaking or motion without becoming solid. If violently shaken it solidifies suddenly; also if an attempt is made to pour it out of the vessel. Of course, the body of solution in which it is placed prevents any noticeable rise of temperature on solidification when dealing with only a small quantity of phosphorus.

I should imagine that chemical action has largely to do with the retention of the liquid condition, bubbles of PH_3 being given off continually, even at temperatures of 8° or 9°C . Still, whatever be the causes, the fact remains that one can obtain and keep phosphorus in a liquid state at such a temperature.—I am, &c.,

E. G. BRYANT, B.Sc.

13, Jubilee Place, Pontefract,
October 8, 1899.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 13, September 25, 1899.

Trimethylene.—M. Berthelot. — Trimethylene and propylene are an example of two gaseous isomers at ordinary temperatures. These substances are similar with regard to their condensation and chemical reactions, but the heat of formation and heat given out during combination differ considerably. The author has studied—(1) The reaction of bromine on the two isomers; (2) the action of zinc chloride on normal propyl alcohol and on trimethylene; (3) the action of sulphuric acid on the propylic alcohols; (4) the comparative reactions of zinc on the two isomeric bromides; and (5) the action of a temperature approaching 500° on propylene and trimethylene. He finds generally that trimethylene is less stable than propylene, and is transformed into its isomer, not only by heat, but even (more or less partially) by the influence of reagents employed for the formation of the bromide. These results, for which the thermo-chemical numbers are given, were predicted.

Journal de Pharmacie et de Chimie,
Series 6, Vol. ix., Nos. 10 and 11.

These numbers contain no matter of chemical interest.

No. 12.

Rectification and Preservation of Chloroform.—V. Masson.—The rectification of chloroform comprises the following operations:—(1) Washing with distilled water; (2) treatment with 2.5 per cent sulphuric acid for two or three days; (3) treatment with 3 per cent soda-lye for three or four days; (4) washing with distilled water; (5) treatment with pure melted coarsely-powdered chloride of calcium; this should be agitated for three or four hours, and poppy-seed oil then added; (6) distillation. Poppy-seed oil possesses to a very high degree the property of preventing the decomposition of chloroform—one-thousandth part of the oil being sufficient to prevent any alteration of the chloroform when exposed to direct solar radiation, while the addition of two-thousandths of poppy-seed oil has kept chloroform intact for three years.

Combination of Phenylhydrazine with Bisulphite of Sodium.—M. Pastureau.—The author has noticed that a solution of bisulphite of sodium gave, when treated with phenylhydrazine, a crystalline precipitate very soluble in water. This precipitate was washed several times with ether, then dried on a porous porcelain plate; it occurs in the form of colourless flakes. By a second crystallisation in water, slowly and carefully evaporated at $50-60^\circ$ the substance was obtained in the form of colourless needles radiating from a centre. Analysis gives the formula $\text{SO}_3\text{Na}, 2(\text{N}_2\text{H}_3.\text{C}_6\text{H}_5)$; it is therefore a double sulphite of sodium and phenylhydrazine.

MISCELLANEOUS

Pelletier-Caventou Monument.—We are surprised to hear from the treasurer of this committee (M. Bocquillon-Limousin, 2 bis rue Blanche, Paris) that until the other day no subscription to the monument had been received from England or any other part of the British Empire. The discoverers of quinine deserve to be honoured by all English-speaking people, for, as M. Bocquillon-Limousin says, "England, by reason of her numerous colonies, should be one of the nations which has profited the most from these benefactors to mankind." This is quite true, and the reason why English subscribers are laggard is that we have not the monument-admiration sense so highly developed as the French. It is not too late to subscribe, and we hope there will still be a response from this side of the Channel.—*Chemist and Druggist.*

On the Identity of α -Digallic Acid and Tannin.—P. Walden.—Flawitsky has already shown that tannin is dextrogyre; $\alpha_D = +60^\circ$ in aqueous solution. The author is of opinion that tannin is not a definite compound, but a mixture containing a compound in variable proportions, with a higher rotatory power, $\alpha_D = +75^\circ$; α -digallic acid is, on the contrary, inactive; further, it softens at 120° and decomposes at 150° , while tannin melts at $110^\circ-115^\circ$. After considering various properties, the author concludes that tannin and α -digallic acid are altogether different bodies.—*Berichte.*

Influence of the Formation of Salts on the Saponification of the Amides and Ethers by means of Alkalis.—E. Fischer.—The research made by the author on the purine group have led him to the conclusion that the saponification of the amidised or ether salt groups is the more rapid as the compound formed is more neutral; or, in other words, that the formation of a salt retards the saponification. Trimethyluric acid 1.3.9 is attacked much more rapidly than the dimethyluric acids. Cyanuric acid is only partially decomposed when heated in a sealed tube for eight hours to 100° , with normal potash, but isocyanurate of methyl is attacked very rapidly under the same conditions, being transformed into trimethylbiuret, $\text{C}_6\text{H}_9\text{N}_3\text{O}_3 + \text{H}_2\text{O} = \text{C}_5\text{H}_{11}\text{N}_3\text{O}_2 + \text{CO}_2$. This latter body crystallises in benzene in acicular prisms, fusible at 126° , soluble in water and alcohol, but very slightly soluble in ether and ligroin.—*Berichte.*

Estimation of Sulphur in Roumanian Petroleum.—G. Filiti.—Among the most important methods for the estimation of sulphur in organic substances may be mentioned that of Carius, the method of decomposing the substances and their oxidation by chlorate of potash and carbonate of soda, the method of oxidation with binoxide of sodium, &c. All these methods have certain advantages in special cases, but become almost useless when we have to deal with the estimation of sulphur in volatile organic substances, and in which the quantity of sulphur is extremely small. Before succeeding in effecting the estimation of sulphur by his new method, the author had tried all the others without success; he then took up the line indicated by Langbein, who showed, by the combustion of saccharine in a calorimeter, that the sulphur was completely oxidised in the presence of oxygen and of a small quantity of water. He applied this method to the estimation of sulphur in petroleum and other bodies. By this method, long and difficult operations and all causes of error are avoided. The advantages of this method are—(1) The possibility of operating on a quantity of material twenty times greater than can be used by the Carius method; (2) the products obtained only contain traces of nitric acid, the precipitation of the sulphur by chloride of barium is effected in a direct and immediate manner. It must be well understood that in using this method it is absolutely necessary to be certain of the purity of the reagents and of the cleanliness of the apparatus.—*Bulletin de la Soc. Chim. de Paris*, Series 3, vol. xxi., No. 7.

NOTES AND QUERIES.

. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Public Analyst.—Can any reader inform me what the necessary qualifications are for recognition as an Analyst under the Food and Drugs or other Public Health Acts?—B.

MEETINGS FOR THE WEEK.

WEDNESDAY, 18th.—Microscopical, 8, "British Trap-door Spiders." Lantern Demonstration by F. Enock F.L.S., F.R.S.

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OUTLINES OF THEORETICAL CHEMISTRY.

By **LOTHAR MEYER**,

Professor of Chemistry in the University of Tübingen.

Translated by P. PHILLIPS BEDSON, M.A. (Dun.), D.Sc. (Lond. et Dun.), B.Sc. (Vic.), F.I.C., F.C.S., Professor of Chemistry in the Durham College of Science, Newcastle-upon-Tyne; and W. CARLETON WILLIAMS, B.Sc., F.I.C., F.C.S., Professor of Chemistry in the University College, Sheffield.

With a Preface by the Author.

. In preparing a second edition of the translation of Meyer's "Outlines of Theoretical Chemistry," the translators have availed themselves of the second edition of the German, published in 1893, a few years before the death of Lothar Meyer. Whilst the original form has been still retained, they have, by occasional footnotes and appendices, sought to bring the book up to date.

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SOME EXPERIMENTS

TO OBTAIN, IF POSSIBLE, DEFINITE ALLOYS OF PLATINUM AND PALLADIUM WITH CADMIUM, ZINC, AND MAGNESIUM.*

By Professor HODGKINSON, Captain WARING, R.A.,
and
Captain DESBOROUGH, R.A.

THAT platinum alloys with zinc has been noticed by several observers ("Gmelin-Kraut," [3], 1193, refers to Gehlen, Fox, Murray, and others; Deville and Debray, *Ann. Chim. Phys.*, [3], lvi., 430; Boussingault, *Ann. Chim. Phys.*, [3], liii., 420).

Generally it is stated that the metals unite with energy, and that when the combination is heated until infusible the compound is representable by the formula Pt_2Zn_3 . Deville and Debray, after heating the zinc alloy with dilute sulphuric acid, obtained a black powder containing 31 per cent zinc and a little free platinum.

Our method has been to submit a weighed amount of platinum to the vapour of the volatile metal, maintaining the platinum and compound formed all the time at a temperature above the boiling-point of the particular volatile metal.

Two plans have been tried: one carrying the vapour with hydrogen, another heating the metals in a vacuum. In both cases a very infusible Jena glass tube was employed.

In each form of experiment a weighed quantity of platinum (or palladium), in thin foil, was contained in a porcelain boat. Almost touching this was another boat containing the volatile metal in very considerable excess. The region about the two boats was heated very strongly in a powerful combustion furnace, and in the case where hydrogen was used the current of gas passed over the zinc, or other metal, towards the platinum.

When the heating was conducted in a vacuum, the Sprengel pump was attached at the platinum end of the tube, so that the vapour could be drawn over the platinum. The heating was in each case continued for some hours (three to four). After cooling, the boat with platinum alloy was weighed.

Cadmium.—*Vapour carried by Dry Hydrogen.*—The alloy or compound formed corresponds almost exactly to the formula $PtCd_2$. This is given by the amount of cadmium taken up by the platinum. (In one experiment, 0.5832 of platinum absorbed 0.6892 cadmium).

The relative weight of the compound at 15° was found to be 13.53, and the calculated for an alloy of the composition $PtCd_2$ is 13.59.

The alloy is white, crystalline, and very brittle. When heated to full redness in a vacuum tube, scarcely any cadmium was sublimed; the loss in weight was inappreciable.

In nitric acid some platinum was dissolved along with the cadmium. Heated in a vacuum tube, the same compound is formed.

Platinum and Zinc in Hydrogen.—The action was slower than with Cd. In one experiment 45.57 per cent of zinc was absorbed. This was a particularly long exposure—nearly five hours—and the temperature was not much above the melting-point of the zinc. An alloy $PtZn_2$ requires 40 per cent Zn. On heating this 45 per cent alloy for two hours in a vacuum tube some zinc was distilled off, leaving a residue containing 44 per cent Zn. It

was now heated until the Jena glass tube began to give way. The Sprengel was keeping up the vacuum during the heating. More zinc distilled off, and after two hours of strong heating the residue was found to contain 24.45 per cent zinc; this is nearly $PtZn$, which requires 25 per cent Zn. It seemed hopeless to try further in glass tubes. This alloy is crystalline and extremely brittle, and dissolves in acids similarly to the cadmium alloy. Heated side by side in a vacuum tube the same alloy of platinum and zinc seemed to be formed. The process was very slow, possibly because the zinc vapour travels but a little way alone.

Platinum and Magnesium.—This was the most difficult, as, at the temperature employed, the magnesium vapour is almost entirely absorbed by the glass of the tube and by the porcelain boat. Some magnesium was distilled in a vacuum; this was placed in a porcelain boat lined with MgO , the platinum was placed as close as possible, and the whole was heated until the Mg was melted; a gentle current of very dry hydrogen was then kept up for some hours. An extremely friable crystalline alloy was produced. From the amount absorbed it corresponds very nearly to the formula $PtMg_2$. These experiments are being repeated.

Palladium.—The experiments with this metal and cadmium and zinc have so far failed to give any result. Very little cadmium seems to be taken up by palladium, either when heated in a vacuum or in a current of hydrogen; what little is taken up distils away very easily. It is possible to keep a piece of palladium foil for two hours in cadmium vapour without change. There is a little more tendency for zinc to alloy.

Nickel behaves very much like palladium in this respect. Some electro-deposited Ni foil was heated for several hours in cadmium vapour without appreciable change in weight.

Ordnance College, Woolwich.

IODINE IN SEA WATERS AND FRESH WATERS.

By A. GAUTIER.

THE examination of the air and its dust has enabled me to establish the fact, which has been alternately affirmed and then denied, that iodine is really found in the air, but that it is completely fixed in the organic state in the matter caught by plugs of glass-wool. Sea air contains about thirteen times as much iodine as that found inland; aerial iodine appears thus to come principally from the sea, which is continually giving up, in the form of aqueous dust, a portion of its iodised elements.

I have proved the complete absence of alkaline or alkaline-earthly iodides in the air, even in several hundred litres collected on the surface of the ocean, and this result was not found without surprise, for sea air contains not only the microscopic organisms which abound on and near the surface of the sea, but also the dissolved salts which the winds are continually carrying off in the form of fine spray. It therefore seemed to me that a part of the iodides from the sea water thus carried by the winds should be found either on the glass-wool plugs when the air was filtered, or in the concentrated solution of potash through which it afterwards passed.

What can be the quantity of alkaline or alkaline-earthly iodides thus carried by the winds? It is proportional to their concentration in the superficial sea water. When I attempted to calculate this concentration, according to the already published analyses of sea water, I was immediately stopped by divergences almost as great as those which I met with for iodine in the air. From the time that J. Boussingault declared that it was almost impossible to detect iodine in sea water, and

* Read before the British Association (Section B), Dover Meeting, 1899.

Stephenson Macadam asserted that several gallons were required to find 1/500,000th of a grain, down to Koettstorffer, the last chemist who dealt with this question, and who found 1 m.grm. in 50 litres, the matter has remained entirely unsolved. In fact, not only the presence of iodine in appreciable quantities in sea water still remains uncertain, but even the existence of this iodine in the form of mineral iodides does not rest on any direct proof, although it has been generally admitted by analogy with what occurs with chloride of sodium. The object of the present paper is to show that the water of the open sea, or at least that at or near the surface, *does not contain a trace of alkaline or earthy iodides*; that iodine is always found in easily weighed quantities, but *that it exists entirely in the organic and organised state*—a circumstance which has been overlooked up till now, and to which is due the contradictory opinions expressed on the quantity, and even on the appreciable presence of iodine in sea water.

During fine weather in November, 1898, in the English Channel at 40 kilometres from the coast, I took 12 litres of water with the usual precaution, and treated it in my laboratory in the following manner:—Pure carbonate of potash was added in the cold as long as a cloudiness appeared, then 0.3 gm. to 0.4 gm. of caustic potash; this was then evaporated without filtering, until its salts commenced to crystallise; it was then mixed, before completely cooling, with alcohol, at 83°: this precipitated the greater part of the salts. The alcoholic solution containing the whole of the alkaline or earthy iodides is evaporated, when it is reduced to about one-twelfth of its volume; it is allowed to cool, the solution is neutralised with dilute sulphuric acid: it is then again made alkaline with a few drops of pure potash, and precipitated a second time with alcohol at 90°. The filtered solution is evaporated to dryness, ignited to destroy the organic matter, and the residue taken up with water and filtered. The aqueous solution thus contains, in a very small volume, the whole of the iodine and bromine from the iodides and bromides in the sea water.

To separate the iodine we have recourse to J. Krutwig's method, perfected by Dechan; it consists in distilling the iodobromised solution with a very concentrated solution of bichromate of potash. The iodine *only* passes over completely and from the beginning with the steam, which may be condensed in 1 or 2 c.c. of pure dilute potash. When 10 to 15 c.c. have been distilled, the potassic liquor is supersaturated with dilute sulphuric acid, and the iodine is estimated as has been described for its determination in air.

Now, when we thus attempt to estimate the iodine in 5 litres of sea water, *we do not find a trace*. Further, I feel certain that by following this method we could recover integrally 0.0005 gm., or even 0.0002 gm. of iodine, added in the state of iodide or iodate* in 1 litre of salt water having the average composition of sea water.

Convinced by these experiments of the absence of mineral iodides in sea water, and remembering what I had already noticed with air, it occurred to me that the iodine might exist in the form of organised corpuscles (microscopic algæ, zoogloæ, &c.), or as organic compounds (such as iodised nuclea, spongine, iodothyrene, &c.), iodised principles in which all the characteristics of mineral iodine have become latent.

To decide this question I took up the residue of 5 litres of sea water which remained insoluble in dilute alcohol, and in which I had vainly sought for mineral iodine, and, after having moistened it with concentrated potash, and even adding pure solid potash, I fused the whole in a pure nickel crucible to destroy all the organic matter. Under these conditions an alkaline odour was given off, indicating the destruction of complex nitrated substances. On cooling, the crucible was placed in ice and water added;

it was then carefully neutralised with dilute H_2SO_4 , and precipitated with alcohol at 90°. The alcoholic solution is filtered, the alcohol driven off, and the iodine tested for in the residue. I thus found—

Total organic iodine in 5 litres	..	12.00 m.grms.
That is—		
Total organic iodine per litre	2.40 „

Thus iodine does exist in sea water in an easily weighable quantity, but the iodised matter in this water is quite insoluble in alcohol in the presence of caustic alkalies, and the iodine does not appear until after fusion with potash: this element is thus found in the water, in the latent form, and cannot be detected until all the organic matter is destroyed—then only can it be weighed, and 20 grms. of sea water is sufficient.

But we must go further, and enquire if the iodine is contained in sea water entirely in the form of microscopic algæ, sponges, &c., or whether a part of this element enters into the constitution of an organic substance soluble in water.

To decide this point I carefully filtered 5 litres of very transparent water from the open sea, on a small filter of Sèvres biscuit porcelain. I soon noticed that a semi-organised glutinous material was deposited on the surface of the porcelain comparable to that secreted by many microscopic algæ. This matter was examined by M. Bornet; he found that it was formed of a slimy substance, in which was entangled various organic and mineral *débris*; he also recognised a quantity of vegetable matter, flagellæ, rotifera, but, above all, microscopic algæ of the family of diatoms. This organic deposit did not appear to amount to 0.01 gm. in the wet state.

Iodine was tested for in the portion obtained from 5 litres of sea water. There was found—

Iodine from organic matter in 5 litres	2.60 m.grms.
That is—	
Organised iodine in 1 litre of water	.. 0.52 m.grm.

In its turn the sea water which had passed through the porcelain filter was made alkaline, evaporated, and the iodine estimated. After fusion with potash, as described above, there was found—

Organic iodine dissolved in 1 litre of sea water	..	1.80 m.grms.
--	----	--------------

The result of these estimations shows that 1 litre of water from the open sea contains in the organic and organised forms:—

Insoluble organised iodine	0.52 m.grm.
Dissolved organic iodine	1.30 „

Total iodine per litre	2.32 m.grms.
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It has already been seen that we found 2.40 m.grms. of total iodine per litre of sea water, a figure which confirms these latter results. We may thus conclude:—

1. That water from the open sea, taken at or near the surface, does not contain a trace of mineral iodides.
2. That in this water the whole of the iodine exists in the form of organic compounds.
3. That a part of this organic iodine, about one-fifth, is fixed in the microscopic organisms which live on or near the surface of the water.
4. That four-fifths of the iodine is found in the state of soluble organic compounds.

The iodised organic matter of sea water merits serious study; this I have only just commenced. I have already found that it can be partially separated by dialysis from the salts which accompany it. The part remaining on the dialyser contains a complex organic substance, at once carbonated, nitrated, and iodised, and rich in phosphorus and manganese. Is this substance derived from the algæ which, so to speak, give it off? Or is it, on the contrary, the primitive organic matter from which they

* The iodine of the iodates can be dissolved in dilute alcohol if the solution is made alkaline by potash.

take their birth? This question has not yet been answered.

Partly dissolved in water, and partly fixed by microscopic organisms, these complex iodised and nitrated compounds from the sea accumulate near the shore, and are deposited as foam. After bathing they adhere to the skin by which they are absorbed later on, benefitting us by their specific action. From observations which I have made in the course of this investigation, I find that analogous phenomena occur with bromine; a notable portion of this element is also found in sea water in the organic state.

There remains to be explained whence the organic iodine in sea water comes, as well as that which is fixed in the organisms and that in solution; evidently it can only come from below, either in the form of iodised springs, volcanic emanations, or by solution of submarine rocks. Numerous terrestrial iodised springs are known (Saxony, Toeplitz, Heilbrunn, &c.), and there is no reason to doubt that similar springs exist in the sea. On the other hand, submarine volcanic eruptions have been observed in every ocean: now it has long been established that volcanic products, such as lava, contain iodine; finally iodine exists in granitic and even calcareous rocks, and these become dissolved in the salt water by the action of carbonic acid and corrosion. This mineral iodine dissolved in the deepest parts of the sea disappears in the upper layers, where the action of light permits organisation and life.

But these marine beings, and particularly salt-water algæ, are not the only iodised organisms. I have found that iodine always exists in appreciable quantities in terrestrial and fresh-water algæ. These algæ can only take their iodine from the waters in which they live. This makes us ask in what form this iodine is found, if it also exists in fresh water in the organic state, and, if so, if it has been missed, as in sea water, by the chemists who have attempted to find and estimate it. I will only take two river waters in which the estimation of iodine has already been attempted—that of the Seine and that of the Marne (*Comptes Rendus*, 1850—1855). After having filtered them through porcelain, to separate the organisms, I estimated the iodine in the part collected on the filter, and also in the filtered water after destroying the organic matter in the residue by fusing with potash. The results per litre of water were as follows:—

	Iodine in organisms. M.grm.	Soluble iodine. M.grm.	Total iodine. M.grm.
Seine water	0.0025	0.0025	0.005
Marne water	0.002	0.0011	0.0031

These waters thus contain a small quantity of iodine, partly soluble: towards 1852 M. Chalin announced the presence of iodine in river waters before I did; we obtained almost identical results. As he worked on simply filtered water, and did not take up his residues with melting potash to destroy the organic matter, it follows that the iodine in these river waters is for the most part soluble in the form of alkaline or earthy iodides.

Whence comes the iodine in fresh water? It comes partially from the air, as we have seen that sea air loses 12/13ths of its iodine when over the land. But it comes principally from the earths and rocks over which the water flows. Iodides have been observed in certain calcareous rocks (the jurassic earths near Lyon, dolomite in Saxony and Savoy, the miocene rocks near Montpellier). But it exists especially in the primitive rocks, where the micas and the micaceous rocks contain numerous chlorised, fluorised, and iodised apatites; we know, in fact, that iodine has been extracted commercially from phosphorites, whose origin is these apatites, as well as from the warm sulphurous waters which emerge from these rocks.

The importance of the estimation of small quantities, both in air and water, of an element so active as iodine, admits of no doubt; this body is indispensable to organ-

ised life, but the smallest proportions suffice. We know that the total extirpation of the thyroid gland, which in man contains no more than 30 m.grms. of iodine, is rapidly followed by death, but that it suffices to leave the patient an insignificant quantity of this gland to maintain its normal function. The influence of small quantities of iodised organic matter on our system is not more mysterious than that of the infinitesimal quantities of silver and copper which destroy life in certain moulds and algæ, or the imponderable amount of zinc necessary to the development of *Aspergillus niger*. Facts of this kind occur in the case of living beings with respect to manganese, iron, fluorine, &c. It is therefore necessary in physiological problems to use the most delicate methods of analysis. In the case of iodine it should be sought for in foods and in water, more especially in all sulphurous, chloridised, and ferruginous mineral waters, where the existence of organic iodine might falsify the results.—*Bull. Soc. Chim.*, Series iii., vol. xxi., No. 12.

LIQUID AIR AS AN ANALYTIC AGENT.*

By Professor DEWAR, M.A., LL.D., F.R.S.

THE increasing importance of low-temperature research is shown by the gradual development of the applications of liquid air for scientific and other purposes. The much larger apparatus now used in the production of the liquid enables experiments to be made on a more imposing scale.

Liquid air poured from a tin can, filled by being dipped into a 5-gallon jar filled with the liquid, into a large silver basin heated to redness, remained apparently as quiescent at this high temperature as in cooler vessels, and maintained a spheroidal condition, just like other liquids. The temperature of the liquid air was about -190° C., or 83° absolute, while the vessel in which it was placed had a temperature of 800° C., or 1073° Ab. In other words, between the wall of the silver vessel and the liquid air there was a difference of temperature of 1000° C., twelve times the absolute temperature of the liquid.

Liquid air can be of great service in the qualitative separation of mixtures of gases. With the object of ascertaining the proportion of any gas in air that is not condensable at about -210° C. under atmospheric pressure, or is not soluble in liquid air under the same conditions, a series of experiments was made with the following apparatus:—

A cylindrical bulb of a capacity of 101 c.c., marked B in figure, had a capillary tube sealed into it terminating in a three-way stopcock, as shown at E. The parts marked C and D consist of soda-lime and sulphuric acid tubes for removing carbonic acid and water. The stand marked G holds the large vacuum test-tube into which B is inserted, and which contains liquid air maintained under continuous exhaustion. As this low temperature had to be kept steady from one to two hours, while at the same time the bulb B had to be completely covered with liquid air, it was necessary to arrange some means of keeping up the liquid air supply without disturbing the apparatus. The plan adopted is shown at H, which is a valve arrangement which can be so regulated as to suck liquid air from the large vacuum vessel A, and discharge it continuously along a pipe into the vacuum test-tube G, the latter being kept under good exhaustion. In working the apparatus, the tube I is connected to a gasometer containing 10 cubic feet of air, so that the volume of air condensed in each experiment may be observed. This was generally from $2\frac{1}{2}$ to 3 cubic feet. If there is a very small proportion of some substance not liquefiable or soluble in liquid air, then we should expect the vessel B would not fill up com-

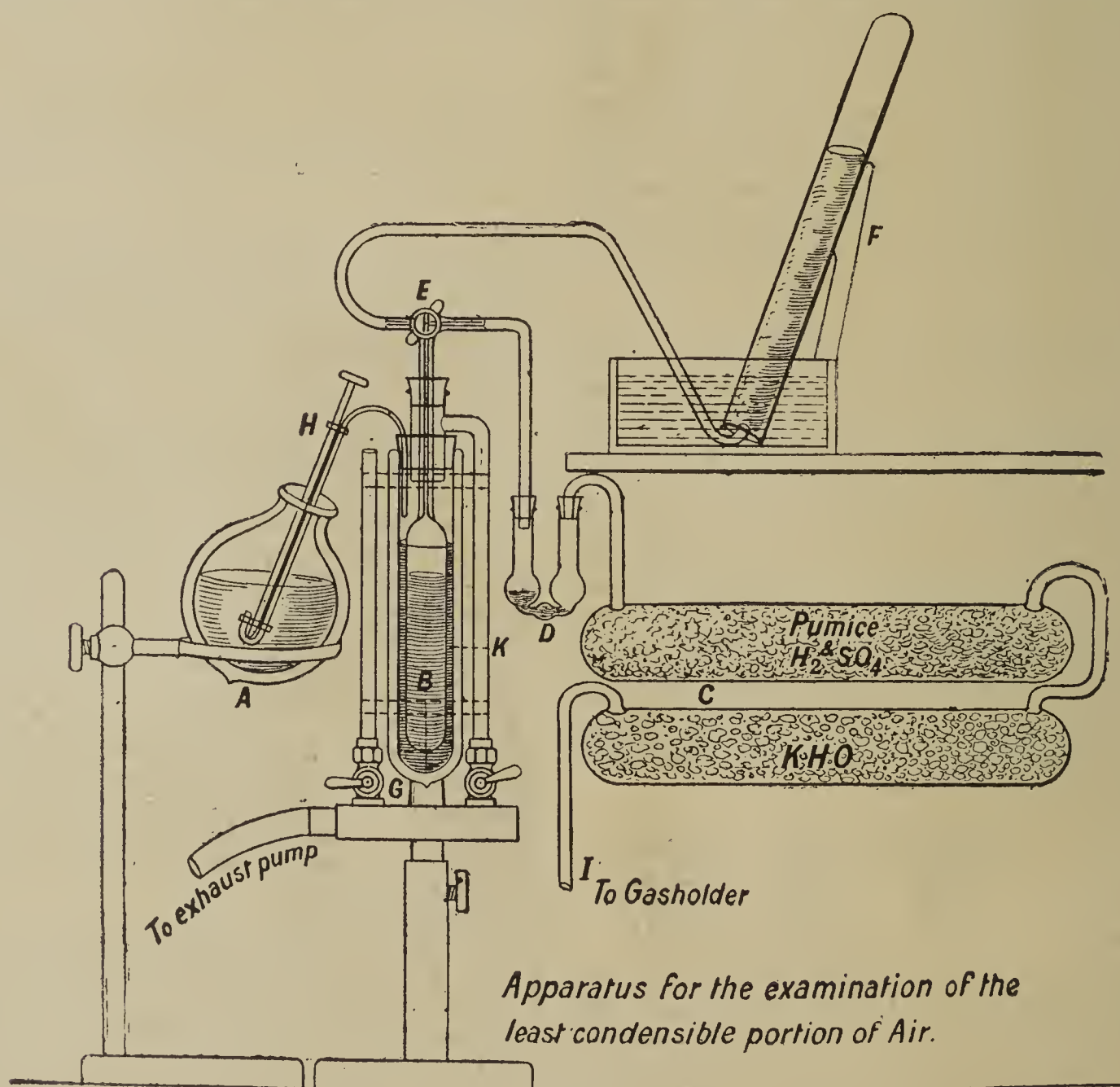
* A Lecture delivered before the Royal Institution of Great Britain, April 1, 1898.

pletely into the capillary tube. This is, however, exactly what does take place. After forty minutes' cooling, the vessel B and the cool part of the tube were filled with liquid. In this experiment some 80 litres of air were condensed, and any accumulated uncondensed matter must have been concentrated in the upper part of the capillary tube, which had a volume of 0.5 c.c. Under the conditions, therefore, the material looked for must be less than 1 part by volume in 180,000 of air.*

To test the working with an uncondensable gas added to air, a volume of 10 cubic feet was taken in the gas-holder, and to that 500 c.c. of hydrogen were added. This is in the proportion of less than 1 in 500. Even after two hours' cooling, the tube B could only be filled four-fifths. In order to prove that the gas accumulated in the upper part of B was hydrogen, the three-way stopcock at E was turned, and the temperature allowed to rise, so

c.c. of liquid air at from -200° to -210° C. had dissolved nearly all this gas; in fact, that 20 c.c. of hydrogen at the low temperature is dissolved in 100 c.c. of liquid air, and can only be detected by examining the first sample of gas boiled off or extracted by lowering the pressure on the liquid. In the Paper on "The Liquefaction of Air and Research at Low Temperatures" (*Proc.*, 1895, xi., 221), it was shown that if hydrogen containing a small percentage of oxygen were employed for the purpose of getting a hydrogen jet, the liquid collected from it was oxygen, containing, however, so much hydrogen dissolved in it that the gas coming off for a time was explosive.

Coal-gas, which is a mixture of hydrogen, marsh-gas, carbonic oxide, and various illuminating gases and impurities, after passing through a coil of pipe surrounded with carbolic acid for the purpose of condensing the vapours of benzol, naphthalene, &c., when supplied to a



Apparatus for the examination of the least condensable portion of Air.

FIG. 1.

that the gas was expelled from the evaporation of the liquid air and collected over mercury as shown at F. The gas thus collected was easily combustible and consisted chiefly of hydrogen. The amount of hydrogen was then reduced to 1 part in 1000 of air, and it was found that after one-and-a-quarter hours' cooling the bulb B had filled to within a $\frac{1}{2}$ c.c. of the capillary tube. A new sample of air, containing 1 part of hydrogen in 10,000 of air, filled the bulb B completely as if it were ordinary air.

It appears from these experiments that 1 part of hydrogen in 1000 of air is just detectable in the form of an uncondensable residue. As the 80 litres of air condensed contained some 80 c.c. of hydrogen, it appears that 100

tube similar to B, surrounded by boiling liquid air, gave a liquid and gaseous portion at the lowest temperature. It was possible to condense in this way all the constituents of coal-gas, and to separate them after liquefaction by fractional distillation, except carbonic oxide and hydrogen.

Ultimately, however, the carbonic oxide would be condensed, and hydrogen be left alone in the gaseous state. Similarly, any gas less easily condensed than air could be separated from a mixture of the same with air. Hydrogen present in air to the extent of one in a thousand is just detectable, but smaller quantities escape direct observation owing to solution in the liquid. In order to press this inquiry a little further, some natural gas known to contain a different constituent, like helium, suggested itself as being worthy of trial. Lord Rayleigh's analysis of the gas from the King's Well, at Bath, gave 1.2 part of helium per 1000 volumes, so that it seemed admirably adapted for such experiments. By the kind permission of

* These experiments, along with the succeeding ones on Bath Gas, were all described in a Paper entitled "Liquefaction of Air and the Detection of Impurities," given at the Chemical Society on November 4th, 1897.

the Corporation of Bath, an abundant supply of this gas was obtained for experimental purposes.

In a paper read before the Royal Society on December 19th, 1833 (*Roy. Soc. Proc.*, iii., p. 254), by Dr. Daubeny, Professor of Chemistry at Oxford University, on the "Quantity and Quality of the Thermal Springs of the King's Well in the City of Bath," there are some interesting details. Dr. Daubeny's experiments extended over a month, and he estimated the volume of gas given

Thirty-two years after Daubeny's experiment Professor Williamson made a more elaborate examination of the Gases of the King's Well. In B.A. Reports, 1865, he gives the following as the volume composition of the gas:—

Carbonic acid.	Oxygen.	Marsh gas.	Nitrogen.
2.948	0.54	0.18	96.33
3.056	0.617	0.216	96.11

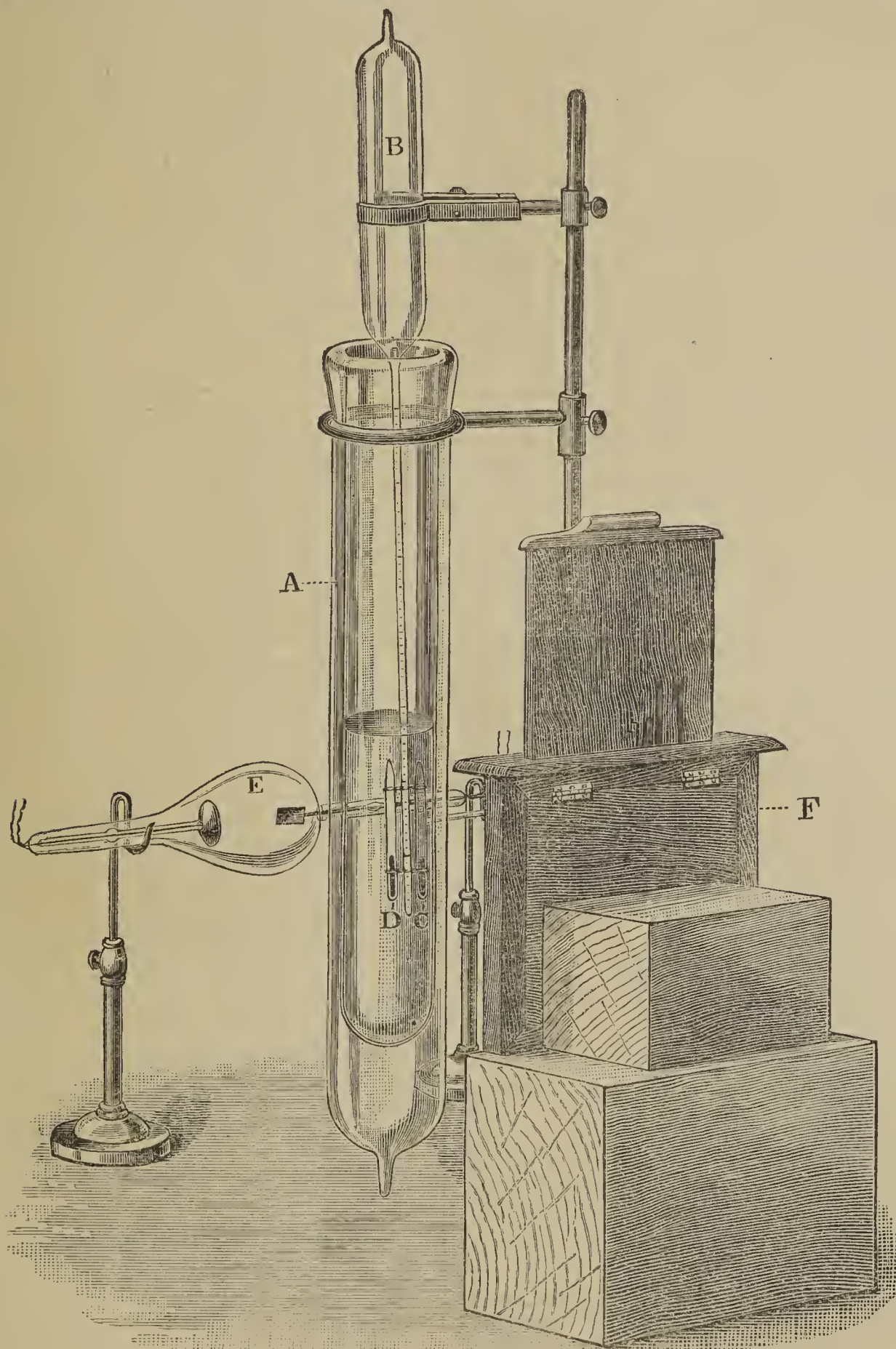


FIG. 2.

A, glass vacuum vessel, containing liquid air. B, tube of argon. C, tube of liquid chlorine. D, tube of metallic sodium. E, Röntgen X ray bulb. F, photographic plate behind sheet aluminium.

off as from 80 to 530 cubic inches per minute (average 264). The temperature of the water of the King's Well was 115° Fahr., and the amount of water per minute was equal to 126 gallons. The average volume of gas was 240 cubic inches per minute. The gas was collected from an area of 20 feet in the centre of the bath; the maximum amount of gas obtained was 300 cubic inches, while the minimum quantity was 194 cubic inches per minute. Calculated at the rate of evolution of 250 cubic feet per day for 5000 years, then the whole gas given off amounts to 456 million cubic feet.

Williamson used a funnel 3ft. 9 ins. in diameter to collect the gas, and obtained a quantity equal to a rate of 112 cubic feet per day. This is only about half the amount Daubeny collected, and may be explained by the great alterations made in the bath itself between the dates of the observations.

In passing, it is interesting to note the general character of the saline constituents of the spring, as the most probable hypothesis is that the argon and helium come from the rocks traversed by the water. The following analysis was made by Dr. Attfield:—

	Grs. per gallon.
Carbonate of calcium	7.8402
Sulphate of calcium	94.1080
Nitrate of calcium	0.5623
Carbonate of magnesium	0.5611
Chloride of magnesium	15.2433
Chloride of sodium	15.1555
Sulphate of sodium	23.1400
Sulphate of potassium	6.7020
Nitrate of potassium	1.0540
Carbonate of iron	1.2173
Silica	2.7061
	<hr/>
	168.2898

Ramsay, the geologist, estimated the mineral ingredients obtained from this source in one year would equal a square column 9 feet in diameter and 140 feet high. Roscoe detected by spectroscopic examination the presence of lithium, strontium, and copper. The sample of Bath gas examined by Rayleigh contained scarcely any oxygen and but little carbonic acid. The weight in a given globe of the N from the Bath gas (2.30522) is about half-way between that of chemical nitrogen (2.299) and "atmospheric" nitrogen (2.3101), suggesting that the proportion of argon is less than in air, instead of greater, as had been expected. Later experiments by Rayleigh proved that this nitrogen contained helium as well as argon.

The sample of gas from the Bath Spring was treated exactly in the same way as the hydrogen mixtures before referred to. During liquefaction there was a marked difference in the appearance of the liquefied gases, for while the hydrogen and air mixtures on condensation gave clear transparent liquids, the product from the Bath gas was turbid, and a precipitate gradually formed which by transmitted light looked yellowish-brown. The yellowish-brown precipitate is a hydrocarbon, probably of the petroleum series, having a marked aromatic smell, and is liquid at the ordinary temperatures. It was probably this gas which Professor Williamson gave as marsh-gas in his analysis. Further research will be made on this substance. Another peculiarity of the liquid nitrogen obtained from Bath gas is that, on examining it with a spectroscope, even through a thickness of 2 inches of liquid, no trace of the characteristic oxygen absorption spectrum could be obtained. In all other attempts to make nitrogen for liquefaction on the large scale, oxygen could always be detected in the liquid by means of its absorption spectrum. Another phenomenon was that the gas from the King's Well could not be entirely condensed by refrigeration with liquid air boiling *in vacuo*. After the cooling had continued for some time, the gas ceased to flow into the condensing vessel, and the upper part of the vessel was occupied by a gas that would not undergo liquefaction at the temperature together with substantially liquid nitrogen saturated with the said gas.

About 70 litres of the Bath gas were condensed, certainly the largest quantity of this gas ever subjected to chemical examination. This was boiled off, and as by accident too much nitrogen had volatilised along with the gas, oxygen was added, and the mixture sparked over alkali, to get rid of the excess of nitrogen. The sample of gas directly collected from the liquid nitrogen contained about 50 per cent of helium. During the sparking the helium lines were well marked (along with others, the origin of which must be settled later), and a vacuum tube filled with the product of the sparking, gave a splendid spectrum of the gas. The recorded unknown lines in the Bath helium were subsequently detected along with helium in the more volatile portion of liquid air (see *Nature*, vol. lviii., p. 570, Letter of Sir William Crookes, Oct. 11, 1898), Eight months after my paper to the Chemical Society, and some two months after this Address was delivered, the same material was found by Professors Ramsay and

Travers to exist in argon, and has been recognised and named by them Neon, a new element.

It is therefore possible to separate helium from other gases by liquefaction when it is only present to the extent of 1 part in 1000. From this it would appear that helium is less soluble in liquid nitrogen than hydrogen in liquid air, and is of greater volatility than the constituents of the other gases which were condensed. If the sample of the uncondensed gas from the first liquefaction of the Bath gas were again treated in the same way, a much more concentrated specimen of helium could be obtained. Provided helium were wanted on a large scale, then a liquid air apparatus, similar to that in use at the Royal Institution, transported to Bath, and worked with the gas from the King's Well, could be made to yield a good supply, as the gas contains 1.2 parts in 1000.

Argon, which is present in the proportion of 1.4 per cent, condenses with the nitrogen; but if the liquid be allowed to slowly boil away, a residuum may be obtained containing about 7 per cent of argon. Argon, when frozen, solidifies to a perfectly clear glass.

Absorption of Röntgen Radiation at Low Temperature by Different Bodies.

The transparency of bodies to the Röntgen radiation is an interesting study, although we are not in a position to draw definite conclusions from the results. As a general fact we know the opacity of elements in the solid state increases with the atomic weight.

In the experiments small tubes of the same bore were filled respectively with liquid argon and chlorine, potassium, phosphorus, aluminium, silicon, and sulphur, and exposed at the temperature of liquid air (in order to keep the argon and chlorine solid) in front of a photographic plate shielded with a sheet of aluminium to an X-ray bulb (see Fig. 2). The order of increasing opacity of the shadow of each substance was observed, and the sequence in the list given above represents the results. A tube containing silicon was a little more transparent than the potassium or chlorine. Sodium and liquid oxygen and air, nitrous and nitric oxides, proved much more transparent than chlorine. Tubes of potassium, argon, and liquid chlorine presented no very marked difference of density on the photographic plates.

From these experiments it would appear that argon is relatively more opaque to the X-rays than either oxygen, nitrogen, or sodium, and that it is on a level with potassium, chlorine, phosphorus, aluminium, and sulphur. This may be regarded as supporting the view that the atomic weight of argon is twice its density relative to hydrogen.

(To be continued).

Reductions in the presence of Palladium.—H. Zelinski.—The author has had recourse to reduction in the presence of palladium for transforming the derived iodides and bromides of the cyclic alcohols into carbides: to effect this, zinc turnings are cleaned with alcohol, then with dilute sulphuric acid, and washed with water; the zinc is then placed in water, and a solution of chloride of palladium (1 to 2 per cent) slightly acidulated with hydrochloric acid is added. The zinc becomes coated with a black adherent layer of palladium; the Zn—Pd couple is placed in a flask and partially covered with alcohol; saturated hydrochloric acid at 0° is then added drop by drop. The hydrogen is at first completely absorbed by the palladium, but, when it commences to come off, a reflux condenser is fitted to the flask, and, alternatively, small quantities of alcoholic iodide or bromide, and hydrochloric acid, are added, avoiding violent action. The return is from 70 to 75 per cent.—*Berichte der Deutschen Chemischen Gesellschaft*.

ON THE INJURY TO AGRICULTURAL LAND
ON THE COAST OF ESSEX
BY THE INUNDATION OF SEA-WATER
ON NOVEMBER 29TH, 1897.*

By T. S. DYMOND, F.I.C., and F. HUGHES.

The Inundation of Sea-water.—On November 29th, 1897, owing to an exceptionally high tide, much of the low-lying land round the coast of Essex was flooded with salt water. In some districts the water drained off the land in a few hours, in others several days passed before it was got rid of, while, where the sea-walls were very seriously damaged, several weeks and even months elapsed before this could be done. So difficult did it prove to repair the breaches in the sea-walls in New England and Peewit Island and in part of the parish of Fambridge that the attempt was abandoned, and many hundreds of acres of land have now reverted to the condition of a salting.

Injury to Crops.—The effect of the salt water upon crops existing at the time of the inundation depended upon the nature of the crop and the length of time it was covered with sea-water. Peas and tares were killed in almost all cases; wheat and turnips did not at first appear to be seriously injured when flooded for a short period, but wheat, where flooded for several days, was killed. Nor did the grasses of permanent pasture appear at first to have received any injury (*Note A*). In the course of a few months, however, when active growth began, the more delicate grasses in the pastures died off, and in only one recorded case was a crop growing at the time of the inundation worth harvesting. This was due to injury to the roots. The water of the North Sea contains 2·7 per cent of sodium chloride (common salt) and about 0·5 per cent of other chlorides and sulphates. Of these, the common salt would be present in sufficient quantities to produce plasmolysis of the root hairs (shrinkage of the cell contents) and therefore serious injury to the plant.

Salt Left in the Soil. Is it Injurious to Crops?—The damage done upon agricultural land by sea-water is variously stated to last from five to twenty years. This is usually attributed to the injurious effect of the salt left in the soil upon crops. To ascertain how far this is the case, a determination of the salt was made in samples of soil taken in January, 1898, from different localities and at different depths (*Note B*). Considerable differences are found in the samples, the amount of salt apparently depending on the character of the soil, the length of time flooded, and the rainfall since the water had subsided. On the average it amounted to 0·25 per cent in the top soil, or twenty-five times more than the average amount in the soil from unflooded land. Now, 0·25 per cent in the top six inches of soil is equal to 2½ tons per acre, which if applied as a top dressing might undoubtedly be injurious to many growing crops. But there is evidence that, if diffused through the soil, a much larger percentage of salt might be present without *directly* affecting plant growth (*Note C*). On the island of Wallasea, wheat which had been sown just previous to the inundation and had not then germinated, when examined in February looked well and strong and the root-action was healthy. At Great Wakering, turnips, the rootlets of which were destroyed by the salt water, were found, after two months, to have sent out fresh rootlets just below the crown of the tap-root, which were entirely uninjured by the 0·3 per cent of salt left in the soil. Mustard, turnips, mangolds, beet, cabbages, peas, creeping-bent-grass, and red fescue were sown in flower pots filled with soil from two of the flooded districts; all germinated well, being apparently absolutely uninjured, even at the most critical period of growth, by the salt left in the soil (*Journal of the Essex Technical Laboratories*, 1898, p. 179).

Effect on the Condition of the Soil.—But while there was no room for doubt that the salt left in the soil was not sufficient *directly* to injure plant growth, its indirect action in spoiling the condition of the soil was equally serious in its effects, and as a result very few of the crops that promised so well in an early stage of growth were worth harvesting. One of the causes of this was the entire disappearance of earth worms, even in land in which they had previously been abundant. (After the inundation the worms were found strewn upon the ground, and were quickly consumed by seagulls). The use of worms in heavy land in assisting the drainage and thus promoting the aëration of the soil is fully recognised, and their extermination was a serious matter; it is only now, nearly two years after the flood occurred, that young worms are beginning again to make their appearance.

But the injury was more far-reaching than this. For some weeks after the flood occurred, although rather moist owing to the power possessed by sea-salt of absorbing moisture and becoming liquid (*Note D*), the soil was in a remarkably good condition, ploughing well, and forming a capital seed bed; the reason for this being that the immediate effect of salt is to granulate gelatinous clay in the same way that salts of lime are known to do. But this condition gradually altered until the soil became difficult to work and in dry weather hard and "cindery." That the clay had now become far more gelatinous than before was shown by mixing the soil with water and allowing it to settle. While that from the unflooded land settled in a few hours, the soil from the flooded land remained suspended for many weeks. As a result of this change, the drainage of water was very seriously retarded, and it was found by experiment that the rate of percolation of water through the flooded soil was only half as rapid as through the unflooded (*Note E*).

Chemical Changes in the Soil.—In order to learn what was the reason for this change in the condition of the clay, some samples of soil were taken from the flooded and unflooded portions of a field at Burnham and the clay separated from each and analysed (*Note F*). It was found that the amount of lime, magnesia, potash, and soda was less by one-fifth in the clay from the flooded than in that from the unflooded land, while, on the other hand, the combined water in the air-dried clay had increased (*Note G*).

Use of Lime.—It must here be explained that clay as it exists in fertile land consists chemically of silicate of alumina combined with small quantities of the silicates of lime, magnesia, potash, and soda, such double silicates being known as "zeolites," and upon the proportion of these bases the fertility of a soil largely depends. When a clay soil becomes impoverished of lime, the double silicates containing lime are decomposed and the clay is left in a highly gelatinous state, which renders the soil unworkable and drainage defective, the aëration of the soil necessary for healthy development of the roots and nitrification of organic matter being impaired. To ameliorate this condition dressings of lime are employed, which by reproducing the double silicates cause the clay to revert to the granular state.

Now, from the results of analysis it is perfectly clear that the effect of the salt has been to eliminate the lime and other bases from the clay (*Note H*), so that it is to this the bad condition of the soil is due. It follows that, to repair this condition, dressings of lime or weathered gas-lime can be used; for, by giving back the lime to the silicates, such an application will cause the re-granulation of the clay, and therefore restore proper aëration and drainage in the soil. In the case of a soil already rich in lime in the form of chalk stones or shells, the soil will gradually recover its condition without the application of lime, but it is likely that even in this case it will greatly hasten its recovery, the lime being in a more active form.

Importance of Cultivation.—While such a treatment will best secure the permanent improvement of the soil, it must not be forgotten that much may be done towards

* Read before the British Association (Section B), Dover Meeting, 1899.

securing a good tilth by cultivation; for, given favourable weather, even gelatinous clay may be dried and rendered temporarily friable by thorough aëration. An examination of the produce of crops on the flooded land (given in the schedule) will show that far and away the best results in 1899 were obtained by fallowing and frequent ploughing in 1898. Anything that assists the opening, aëration, and drainage must be beneficial on the flooded land. At Great Wakering, the effect on a crop of turnip seed of—(1) farmyard manure, (2) sewage cake, and (3) long hay manure (obtained from vessels carrying cattle) were compared. As might be expected, the best crop was obtained with the long hay manure and the worst with the sewage cake; the former having best promoted the aëration and drainage of the soil. Hence ploughing in long dung, spoilt hay, and even a white straw crop that is not worth harvesting, should prove most useful.

Elimination of Salt.—And by promoting drainage a further purpose is best served—the elimination of the salt. It is a mistake to suppose the salt will be appreciably diminished by the growth of crops. Even mangolds, which absorb more salt than any other farm crop, would only remove 136 lbs. per acre, whereas the salt in the first 9 inches (if 0.1 per cent) amounts to 3000 lbs. (Note I). Hence it is only by taking advantage of the rainfall and encouraging rapid drainage that the salt can be eliminated. Salt is, of course, very soluble in water, and, unlike some other soil constituents, is not retained by the soil but is always found in drainage water. From an experiment made in the laboratory, it was found that $1\frac{3}{4}$ inches of rain water, when allowed to filter through 6 inches of the soil from the flooded arable land at Wallasea was more than sufficient to remove almost every trace of salt. In the field, however, it must be remembered that while, during wet weather, salt is washed downwards, during dry weather, owing to evaporation of water from the surface of the soil, there is a movement of salt upwards, so that the complete elimination of the salt would require a much greater rainfall than the foregoing experiment indicated. The total rainfall for the eighteen months from December 1st, 1897, to May 31st, 1899, was $26\frac{3}{4}$ inches (Note K), and to ascertain how far this had washed the salt from the flooded land a second series of determinations was made last June. It was found that in almost every case the salt had been very materially reduced, in some instances to one-tenth, and on the average to one-quarter, of the amount present in the beginning of 1898. This must be considered a satisfactory result, and if care is taken to keep the drains open and to run off the salt water as it collects in the dykes, a reasonably heavy rainfall during the coming winter should effectually remove the remaining salt (Note L).

Impoverishment of the Soil.—It has already been pointed out that the chemical action of the salt upon the clay of the flooded soils has resulted in the elimination of a part of the lime, magnesia, potash, and soda, which have been converted from the form of insoluble silicates into soluble muriates. The effect of the inundation was, therefore, greatly to increase the supply of available plant food. That this was the case was shown by a determination of the available constituents in the Burnham soil (Note M), the clay of which had been previously analysed for the total constituents. It was found, for example, that while the total potash in the clay had been reduced from 1.12 to 0.84 per cent by the action of the salt, the soluble or available potash in the whole soil was increased from 0.025 to 0.079 per cent, and not only the available bases, but the available phosphates also had been increased in quantity. But while the rendering soluble of these constituents has increased the available plant food, it must also have given rise to considerable loss by drainage, so that the total quantity of the constituents has been reduced.

Artificial Manures.—It is therefore clear that the effect of the inundation has been very materially to impoverish the land, but that owing to the large increase in the

availability of the remaining constituents, there is abundant mineral plant food for the immediate needs of crops, and that, therefore, potash and phosphatic manures are likely for some time to come to prove less beneficial than upon land that has not been flooded. This remark does not apply to nitrogen; for, owing to the inefficient aëration of the soil, the production of nitrate must have been retarded, and in the event of the soil being in such a condition as to allow a luxuriant crop, a dressing of nitrate of soda should prove useful for cereal and root crops, and especially permanent pasture. For crops upon which phosphatic manures are specially required, basic slag should be used in preference to superphosphate, both because the salt still present possesses a solvent action for the slag, and because the lime of the slag is itself useful—the acid of superphosphate injurious—to the condition of the clay.

Crops.—With regard to the crops best adapted to cultivation on the flooded land, much information may be gained from the experience of farmers during the past two years tabulated in the schedule (Note N). It is clear that success depends more on the condition of the land than upon the particular crop selected for cultivation. Wheat, barley, oats, and mangolds have all given a fair yield in some cases, and in others have entirely failed. Rye-grass, however, which was expected to answer, even if other crops did not, has in some cases failed to germinate, and in all proved disappointing, and instead a rank growth of twitch and squirrel-tailed grass and other weeds has appeared. But there is one class of crops which has proved almost uniformly successful, namely, the cruciferous. At Mundon, on the flooded land, a larger crop of kale was obtained in the autumn of 1898 than had ever been given on the farm before; on the enclosure at Tillingham, where all the crops had failed, rape, among other self-sown plants, was growing strong and vigorous in the spring of 1899; at Burnham, on land sown with rye-grass, the soil last winter became smothered with charlock; on Foulness, mustard gave a good half crop in 1898, and at Dengie nearly an average crop in 1899; while at Wakering, turnip seed sown in 1897 gave a good half crop in the spring of 1898, and was the only recorded case of a crop which, submerged by the salt water, was worth harvesting. There can be little doubt that, on land where other crops fail, one or other of the cruciferous crops will be found to succeed.

In conclusion, we wish to express our indebtedness and hearty gratitude to Messrs. E. A. Fitch, J. Grainger, J. C. Chillingworth, Wm. Sewell, E. J. Smith, A. B. Croxon, A. W. Croxon, E. A. Wedd, S. W. Squier, A. M. Clarke, W. H. Vellacott, G. H. Cross, F. D. Girling, P. Stanford, and other gentlemen for the help and information they have afforded and which has enabled us to prepare this report.

NOTES:

A. According to Longfellow, the French farmers of Nova Scotia purposely allowed their meadows to be periodically flooded with salt water:—

“Dikes that the hands of the farmers had raised with labour incessant
Shut out the turbulent tides; but at stated seasons the flood-gates
Opened, and welcomed the sea to wander at will o’er the meadows.”—*Evangeline*.

Arthur Young, in his “General View of the Agriculture of Essex” (p. 13) published in 1813, states that “forty years ago the whole of one of the islands on the Essex coast was under water and no corn got for two years; but after that much greater than ever, so as to furnish an effectual proof that (salt) water did good, after being chastened and corrected by the atmosphere.”

B. The soils of Foulness, Great Wakering, and Tillingham are heavy alluvial soils overlying sand, the last-

mentioned being distinguished by a layer of sea-weed ($\frac{1}{4}$ th inch) separating the top soil from the sandy subsoil. Those at Northey Island, Burnham, and Wallasea are heavy soils on a clay subsoil. At West Thurrock the soil is a deep heavy alluvial soil overlying peat; the land is not drained. The first series of samples, with the exception of that from Great Wakering, were taken for analysis in January, 1898, and it is noticeable that the rainfall since November, 1897, had been even then sufficient to wash most of the salt into the subsoil, except in the case of West Thurrock, where the land was flooded for eight weeks, and no rain had occurred after the salt water had drained off before the samples were taken. At Great Wakering, the samples were taken a month later, and the salt had, by evaporation of water, been again carried upwards. The second series of samples were taken in May, 1899.

C. Interesting facts upon this subject were deduced during the reclamation of Lake Aboukir in Egypt (*Minutes of the Proceedings of the Institute of Civil Engineers*, 1890, ci., pp. 189—204). This lake had an area of 30,000 acres, and was $3\frac{1}{2}$ feet below sea-level. It is known to have been flooded with sea-water in 1715. Since then it has been flooded by the Nile each year in winter and evaporated every summer, a deposit of pure white salt, 3 or 4 inches in thickness being deposited in the depressions. The soil from the bed of the lake was found by Dr. Voelcker to contain from 8 to 9 per cent of sodium chloride, and to reclaim it, 450 tons of salt had to be extracted from each acre. The methods adopted in Egypt to reclaim salt land are—(1) By warping until a sufficient depth of silt is produced to grow crops; (2) by washing *up* the salt by continuously passing fresh water over the land; (3) by washing the salt *down*, the land being flooded with fresh water and dykes cut, into which the water drains through the soil. The last method was adopted in the case of Lake Aboukir, and after one year's washing, the salt was reduced to 0.5—2 per cent at a depth of 12 inches. It was found that when the soil contained 2 per cent of salt, crops of annual grasses grew 2 feet in height, and when further reduced to 1 per cent full crops, 4 feet high, were obtained. When the salt was reduced to 0.5 per cent good crops of rice and clover could be grown. The fertile soil in the neighbourhood contains 0.01 per cent of salt. Upon the higher portion of the bed of the lake, the soil contained 1.6 per cent of salt before reclamation, and upon these, scrubby crops of barley were annually grown.

D. This is due to the chlorides of magnesium and calcium which are contained in sea-water in small quantities; chloride of sodium is not itself deliquescent.

E. This was determined by filling two percolators with the soils and, after saturating with water, noting the time taken for each c.c. of water to percolate through:—

	Flooded.		Not flooded.	
First c.c. of water occupied	16	minutes	8.3	minutes.
Second	15.8	"	8.4	"
Third	16.2	"	8.4	"
Fourth	16.7	"	8.5	"
Fifth	16.9	"	8.6	"
Sixth	16.7	"	8.6	"
Seventh	17.4	"	8.7	"
Mean	16.5	"	8.5	"

An experiment was also made on the retentivity of the soil for water. It was found that 100 grms. of the air-dried soil from the—

	Expt. 1.	Expt. 2.	Mean.
Flooded land retained	40.6	42.0	41.3 grms. of water
Unflooded "	41.7	42.7	42.2 " "

so that the water capacity of the soil had not been greatly altered.

F. For this purpose the samples of soil were mixed with water in a cylinder, and the fine clay removed by a slow stream of water into a large trough, where it was allowed to deposit. The clay thus obtained was exposed to a current of dry air until it ceased to lose weight. The results of analysis were as follows:—

	Clay from flooded land. Per cent.	Clay from unflooded land. Per cent.
Lime	1.23	1.42
Magnesia	1.16	1.54
Potash	0.84	1.12
Soda	0.25	0.37
Phosphoric acid	0.21	0.16
Insoluble sand and clay ..	62.77	61.10

To determine the water of hydration, the air-dried clay was heated to 240° C., the highest temperature at which it could be safely heated without decomposing any organic matter present:—

	Clay from flooded land. Per cent.	Clay from unflooded land. Per cent.
Loss at 240°	7.38	5.34
Further loss on ignition ..	9.48	9.62
Total loss on ignition ..	16.86	14.96

G. It is remarkable that since the inundation occurred, the land frequently becomes coated with a white efflorescence of gypsum (sulphate of lime), no doubt partly produced by reaction of the liberated lime with the sulphates of the sea-water.

H. Professor Way and others have shown that when solution of common salt acts upon zeolites, lime, magnesia, and potash are eliminated, their place being taken by an equivalent quantity of soda. In the case of the flooded land this may very probably have been the first change, especially because it is a substitution which need not alter the physical condition of the clay, and it was observed that the soil worked well for some months after the inundation occurred. But a further change has taken place during the eighteen months that elapsed before the samples were taken—a change which rendered the clay gelatinous and unworkable, and by which the soda has itself been eliminated, it is to be supposed, as carbonate. Gelatinous clay, it is probable, differs from granular clay in consisting of far smaller particles; it is, in fact, colloidal, and this is shown by the permanent suspension of such clay when mixed with water. If a base be removed from an aggregation of molecules to which it is essential, the aggregation will be broken down into, at any rate, smaller aggregations, so that the elimination of the soda would have the observed effect of rendering the clay gelatinous. If in the reaction the soda in the double silicates is replaced by water, this might partly account for the greater loss in weight of the dry gelatinous clay when heated to 240° C. than of the dry granular clay.

I. The principal farm crops absorb on the average the following quantities of salt per acre:—

	Pounds.		Pounds.
Wheat	4	Red clover ..	16
Barley	7	Meadow grass ..	24
Potatoes	7	Swedes	25
Beans	9	Mangolds	136
Oats	10		

K. The monthly rainfall for the eighteen months from December, 1st, 1897, to May 31st, 1899, as observed at Chelmsford was as follows:—

December, 1897 ..	2.02	September, 1898 ..	0.29
January, 1898..	0.74	October ..	2.32
February ..	0.80	November ..	2.03
March ..	1.38	December ..	2.30
April ..	1.15	January, 1899..	1.81
May ..	1.95	February ..	1.60
June ..	2.21	March ..	0.79
July ..	0.64	April ..	2.32
August ..	0.86	May ..	1.50

L. At Foulness, although the subsoil is sandy and the drainage free, only a small reduction in the amount of salt has taken place. It is to be suspected that this is due to the salt water being allowed to remain in the dykes, so that in dry weather it has been re-absorbed by the soil. The field on Northey Island is a sloping one, and the subsoil is heavy clay; the salt would therefore be washed from the upper part of the field to the lower part from which the sample was taken, so that a material decrease of the salt could not be expected. In this case water furrows should be cut across the field. In the preliminary report it was suggested that until the salt was washed from the surface soil, ploughing should be avoided. As this suggestion has been very strongly criticised, it should be pointed out that the same principle is involved as in the deep cultivation *versus* the deep ploughing of land overlying yellow clay. The object was to prevent the salt from being brought again to the surface. The first object, it was suggested, should be to eliminate the salt, the second to produce a good tilth; but even in February, 1898, the salt was sufficiently washed into the subsoil in most cases for ploughing to be carried on without bringing up much salt to the surface.

M. The available soil constituents were determined by Dyer's method by extracting with a 1 per cent solution of citric acid. The results were as follows:—

	Soil from flooded land. Per cent.	Soil from unflooded land. Per cent.
Lime	0.695	0.791
Magnesia	0.101	0.036
Potash	0.079	0.025
Soda	0.069	0.013
Oxide of iron and alumina.	0.933	0.777
Phosphoric acid.. ..	0.040	0.029
Silica	0.300	0.77

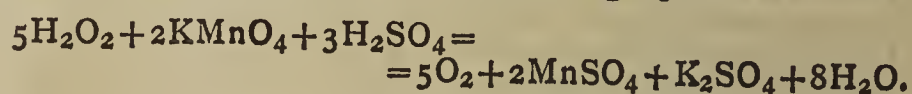
N. Some information respecting the crops that can be best grown on land containing salt may be gleaned from the experience of those who have reclaimed land on the coast. A new enclosure at Tillingham was made in 1871. It was flooded again in 1874. In 1881 a portion of the land was broken up and sown with oats, but these came to nothing and were fed off. In 1882 oats produced a crop of about six quarters an acre, but very light in weight. In 1883 oats did about the same; mustard produced a very light crop. In 1884, wheat gave about three quarters an acre. In 1885, oats gave six quarters. In 1886, wheat, barley, and beans each did fairly well, and the land has been successfully cropped till again flooded in 1897. A new enclosure at Holderness at the mouth of the Humber was reclaimed with much less difficulty. A good growth of grass and abundance of white clover spontaneously appeared in this case within three years of enclosure. On the part of the enclosure intended for arable land, rape was sown the third and fourth years after enclosure, and gave an exceptionally good yield; oats and beans were successfully grown the next season, and wheat the season after (*Minutes of Proceedings of the Inst. of Civil Engineers*, xxi., p. 454). We are informed by Mr. I. J. G. Kakebeeke, of Goes, Holland, that in the case of some land recently flooded with salt water in his neighbourhood, red clover was found to be the most remunerative crop.

COMPARATIVE ACCURACY OF TITRIMETRIC AND GASOMETRIC METHODS OF ESTIMATING HYDROGEN DIOXIDE IN PRESENCE OF VARIOUS PRESERVATIVE AGENTS.*

By CARL E. SMITH.

THE method of estimating hydrogen dioxide most extensively used is that of titration with potassium permanganate. Besides being more readily applied than any other, this method has always been presumed to give accurate results, at least sufficiently so for all practical purposes. Dr. Charles Rice, however, has observed that its accuracy is affected by the presence of glycerin, which some manufacturers add to the solutions to give them stability. A variety of other substances have from time to time been reported to be in use for the same purpose, and it was suspected that at least a part of them might also exert an influence on the results of the method. Such substances are boroglycerin, boric, salicylic, and benzoic acids, acetanilide, salol, &c. It was important, therefore, to know if the inaccuracies introduced by the presence of glycerin or any other of the above enumerated substances are so great as to make the method worthless, and, if so, whether a method could be found that is not affected by these additions, one that could be relied upon under any conditions likely to occur in the assay of commercial solutions of hydrogen dioxide. It was the writer's task, for this purpose, to make comparisons of the more prominent titrimetric and gasometric methods under such conditions as might be encountered in practice. The experiments were confined to four methods, a description of which will first be given.

Titrimetric Permanganate Method.—When a solution of potassium permanganate is gradually added, with agitation, to a solution of hydrogen dioxide containing sulphuric acid, the permanganate is decolourised through the formation of manganous sulphate, and all available oxygen is liberated from the hydrogen dioxide, together with an equal amount from the permanganate. When the last drop of the solution added leaves a permanent red colour after agitation, the reaction is ended. It proceeds in accordance with the following equation:—



If 1 c.c. of hydrogen dioxide solution is taken and a N/10 solution of permanganate used, the number of cubic centimetres required to produce a permanent red colour, multiplied by 0.56, will indicate the number of volumes of available oxygen yielded by one volume of the sample.

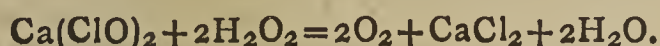
Gasometric Permanganate Method.—The reaction made use of in this method is the same as in the preceding one, the principal difference being in the direct measurement of the liberated oxygen instead of its calculation from the amount of permanganate consumed. The operation is performed in a gasometer, or nitrometer, several forms of which have been devised. A description of the form best suited to this work and its use will be found in the Appendix of the U. S. P. of 1890, under "Gasometric Estimations," and in the Dispensatories. The writer operated in the following manner:—The measuring tube, graduated to 100 c.c., is filled with a saturated solution of sodium chloride, 2 c.c. of the sample are accurately measured into the funnel tube and slowly let into the measuring tube, care being taken that no air is admitted. Ten c.c. of 10 per cent sulphuric acid are then admitted in the same manner, and finally 20 c.c. of a 2 per cent solution of potassium permanganate. When the reaction has nearly ceased, the tube is inverted a few times to in-

* Report from Research Committee D, Section II., of the Committee of Revision of the U.S. Pharmacopœia. From the *American Journal of Pharmacy*.

sure complete decomposition of the hydrogen dioxide. This must be repeated several times within the next five minutes, on account of the voluminous precipitate of hydrated manganese dioxide, which prevents small bubbles of gas from rising to the top. The tube is then placed in a vertical position, and, when the volume of gas becomes constant, the liquid in the equilibrium tube is adjusted to the same level as that in the measuring-tube. The volume of gas is then read and the temperature noted. Since the standard of strength of hydrogen dioxide solutions is *not* based on the volumes of oxygen yielded at ordinary room temperature, but on the volume the gas would occupy at 0° C. and 760 m.m. barometric pressure, a correction is required for accurate determinations. The writer made correction for variation in temperature only, as sufficient for ordinary purposes. The reader is referred to the "Pharmacopœia" for the formula and tables required for this. It should not be omitted, as the error would be quite considerable. A solution yielding 10 volumes of oxygen at 0° C., would yield 10.55 volumes at 15°, 10.75 volumes at 20°, 10.9 volumes at 25°, &c.

In the writer's hands this method does not give very encouraging results. Duplicate estimations differ much more than with other methods, the precipitated manganese dioxide collects near the top of the liquid, and makes a close reading of the volume impracticable, besides obstructing the passage of gas bubbles. While not entirely worthless, it is much less satisfactory than the following method.

Gasometric Hypochlorite Method.—This method is recommended by D. B. Dott (*Ph. J. Tr.*, 1890, p. 833), who uses a solution of ordinary bleaching powder, also filling the apparatus with it instead of sodium chloride solution. Mr. Dott obtains appreciably higher results than by titrimetric methods, and concludes the method to be more accurate than the latter. The reaction is analogous to that of the permanganate methods, as follows:—



In some of the present writer's experiments a solution of chlorinated soda of approximately U.S.P. strength was used, in others a solution of chlorinated lime containing about 4 per cent of available chlorine. Preference is given to the latter, as with the other a white flocculent precipitate (probably sodium hydrate and carbonate) is formed, which is open to the same objections as that incidental to the permanganate method. A saturated solution of sodium chloride was used in all cases for filling the gasometer. Two c.c. of the sample are admitted into the measuring tube, the funnel tube rinsed with a little water; this also let in, and then 20 c.c. of the chlorinated lime solution added. From this point the procedure is the same as explained under the permanganate method.

With solutions containing in addition to hydrogen dioxide only small quantities of mineral acids and alkali salts, quite satisfactory results were obtained by this method; but in the cases of solutions to which any of the various preservatives had been added, there was a decided tendency, almost throughout, toward too low results. No appreciable error seems to be introduced through the solubility of oxygen in the liquid, above which the gas is collected, as no higher results were obtained when the liquid had previously been saturated with oxygen.

(To be continued).

Truro Sewage Scheme.—The Corporation of this city have unanimously agreed to consult Mr. Candy, of the International Purification Syndicate, 109, Victoria Street, Westminster, with regard to the treatment of the sewage of Truro upon the system of purification by Bacteria beds, which dispenses with the necessity of septic tanks and coke filters.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 14, October 2, 1899.

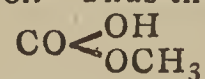
Two Chlorobromides of Tungsten.—Ed. Defaçon.—The author finds that it is not possible to prepare hexabromide of tungsten by the action of liquid hydrobromic acid on the hexachloride in sealed tubes kept at a temperature of 70°, but he has prepared two chlorobromides: one, the more stable of the two, is formed at about 70°, and is the hexachloro-trihexabromide, $\text{WCl}_6.3\text{WBr}_6$; the other is obtained at a temperature of 15°, and is the hexachlorobromide, $\text{WCl}_6.\text{WBr}_6$. These two compounds are the first known chlorobromides of tungsten. The former substance is green, and composed of a mass of small crystals which melt at 232°; on exposure to air, it rapidly alters, turning brown in colour.

Hypophosphite of Copper and its Decomposition by Precipitated Palladium.—R. Engel.—The author has succeeded in preparing copper hypophosphite, a substance which hitherto had not been obtained owing to the facility with which hypophosphorous acid reduces copper salts. The preparation consists in precipitating a solution of copper sulphate by the molecular equivalent of a solution of hypophosphite of barium. The precipitated sulphate of barium can be filtered off, and the solution can be evaporated in air over sulphuric acid. The solid salt is white, and when anhydrous has the formula $(\text{PO}_2\text{H}_2)_2\text{Cu}$. Precipitated palladium decomposes copper hypophosphite in the cold, metallic copper being deposited and hydrogen evolved. The reaction is represented by the equation $(\text{PO}_2\text{H}_2)_2\text{Cu} + 2\text{H}_2\text{O} = \text{Cu} + 2\text{PO}_3\text{H}_3 + \text{H}_4$.

Salicylic and Para-oxybenzoic Aldehydes and Salicylhydramide.—MM. Delépine and Rivals.—During the thermo-chemical investigation of the derivatives of salicylic aldehyde, the authors have obtained results incompatible with previous determinations. Therefore they have measured again the heat of formation of salicylic acid and aldehyde, besides that of paraoxybenzoic aldehyde, of salicylhydramide, with many control experiments.

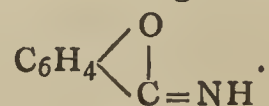
Berichte der Deutschen Chemischen Gesellschaft.
December 12, 1898.

On the Compounds of Carbonic Acid with Water, Oxide of Ethyl, and the Alcohols.—W. Hempel and J. Seidel.—A compound of carbonic acid and water, having for its formula $\text{CO}_2 + 8\text{H}_2\text{O}$, has already been described. This compound may be obtained by placing a certain quantity of water in a thick tube, cooling to -80°, and adding carbonic acid snow; the tube is then sealed up and allowed to return to the ordinary temperature. We notice that the contents of the tube separate into two liquid layers, the water below and the carbonic anhydride above. At the same time crystals having the above-mentioned formula are deposited; these melt at 8° at a pressure of 43 atmospheres, and decompose between -2° and +20° at the normal pressure. Carbonic acid snow also dissolves in ether; if it is added to water saturated with ether a white precipitate is obtained; the composition of this substance is variable and depends on the temperature of the mixture. At -50° it is represented by the formula $(\text{C}_2\text{H}_5)_2\text{O} + \text{CO}_2 + 4\text{H}_2\text{O}$. Liquid carbonic acid unites with the alcohols, giving compounds fusible above the freezing-point of alcohol. Thus the compound—



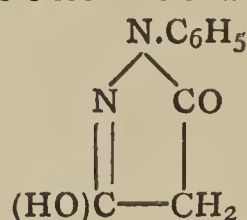
solidifies at -79° and melts at -60°: ethylic ether, $\text{C}_2\text{H}_5\text{O} + \text{CO}_2$ melts at about -61°, and amyl ether at -56°.

The Constitution and Cryoscopic Constants of *o*-Cyanophenol.—K. Auwers and A. J. Walker.—The phenols generally behave in an abnormal manner from the cryoscopic point of view when benzene is used as a solvent; *o*-cyanophenol, on the contrary, is again abnormal and behaves like the para-isomer. Thus it is supposed that it may have the following constitution:—



The authors have attempted to verify this hypothesis experimentally, and have found that *o*-cyanophenol does not exist in two tautomeric forms, and does not give rise to two series of derivatives. They have also studied a series of substitution derivatives of *o*-cyanophenol from the cryoscopic point of view, the results of which are fully described in this paper.

On Phenyl-1-hydroxy-3-pyrazolone-5.—A. Michaelis and H. Roehmer.—The present memoir has for its object the completion of the study of phenylmethylpyrazolidone, and to show that the formula attributed to it should be by preference that of an oxypyrazolone:—



To prepare this body, 1 molecule of chloromalonie ether is mixed with 3 molecules of phenylhydrazin, and allowed to stand for three days, while preventing the access of air. The mass is then dissolved in soda, the solution is washed with ether, then supersaturated in the cold with hydrochloric acid. The yellow precipitate which is formed is drained, washed with water, and re-crystallised in alcohol; we thus obtain bright yellow flakes fusible at 192°. The original oxypyrazolone unites directly with benzoic aldehyde at 130°, giving a benzylidenic compound, which crystallises in reddish needles fusible at 108—109°, and soluble in the usual solvents. If phenyloxypyrazolone (1 mol.) is heated with oxychloride of phosphorus (2 mols.) in a closed vessel to 150° for six hours, it is transformed into phenyl-1-dichloro-3.5 pyrazol, which is purified by a current of steam. This body boils at 170—172° at 16 m.m., and crystallises on cooling in white needles fusible at 25—26°.

Transformation of Geraniol into Methylheptenol.—F. Tiemann.—M. Barbier has, by acting under pressure with alcoholic potash on geraniol, obtained an alcohol boiling at 79° at 10 m.m., to which he gave the name dimethylheptenol. The author shows that this alcohol is identical with the methylheptenol obtained by acting with potash on methylheptenone. The identification was made by means of the physical and chemical properties of the two products. The action of alcoholic potash on linalool under pressure does not give rise to any analogous product.

On Citral (Geraniol) and Essence of Lemon-grass.—F. W. Semmler.—A controversial article on the subject of the identity of citral and the aldehydes obtained from essence of lemon-grass.

January 9, 1899.

Influence of the Formation of Salts on the Saponification of the Amides and Ethers by means of Alkalis.—E. Fischer.—Already inserted.

The Formation of Putrescine from Ornithine.—A. Ellinger.—Ornithine was obtained by Jaffe's method, by hydrating its benzoyl derivative, ornithuric acid, by means of hydrochloric acid. The hydrochlorate of ornithine was dissolved in water, and soda added until slightly alkaline. On infecting this with a little putrid pancreas, and keeping at 30° for three days, CO₂ is given off, and trimethylene diamine can be obtained from the

liquid. This is characterised by its transformation into a benzoylised and chloroplatinate derivative. Ornithine has the following constitution:—



On the Identity of α -Digallic Acid and Tannin.—P. Walden.—Already inserted.

On the Isomeric Benzoylketoximes.—J. Schmidt.—Already inserted.

On the Non-nitrated Products of the Decomposition of Morphine.—E. Vongerichten.—In this paper the author establishes the relations which exist between morphenol and morphol; methylmorphenol, reduced by sodium and absolute alcohol, gives a crystalline phenol easily oxidisable, and which gives an oily acetylated derivative. Now the oxidation of this latter by chromic acid, in acetic solution, leads to a quinone identical with methylacetylmorpholquinone. Morphenol, distilled with zinc powder, gives 50 per cent of phenanthrene.

MEETINGS FOR THE WEEK.

FRIDAY, 27th.—Physical, 5. "Magnetic Properties of the Alloys of Iron and Aluminium," by Dr. S. W. Richardson. Exhibition of a Model illustrating a number of the Actions in the Flow of an Electric Current, by G. L. Addenbrooke. Repetition of some Experiments with the Wehnelt Interrupter devised by Prof. Lecher, by W. Watson.

SECOND EDITION, 8vo, 9s.

OUTLINES OF THEORETICAL CHEMISTRY.

By **LOTHAR MEYER**,

Professor of Chemistry in the University of Tübingen.

Translated by P. PHILLIPS BEDSON, M.A. (Dun.), D.Sc. (Lond. et Dun.), B.Sc. (Vic.), F.I.C., F.C.S., Professor of Chemistry in the Durham College of Science, Newcastle-upon-Tyne; and W. CARLETON WILLIAMS, B.Sc., F.I.C., F.C.S., Professor of Chemistry in the University College, Sheffield.

With a Preface by the Author.

* * * In preparing a second edition of the translation of Meyer's "Outlines of Theoretical Chemistry," the translators have availed themselves of the second edition of the German, published in 1893, a few years before the death of Lothar Meyer. Whilst the original form has been still retained, they have, by occasional footnotes and appendices, sought to bring the book up to date.

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Further particulars on application to the Director—

ALFRED JÖRGENSEN, The Laboratory, Copenhagen, V.

UNIVERSITY COLLEGE, LONDON.

THE MANIPULATION OF GASES.

By **MORRIS W. TRAVERS**, D.Sc.

A Course of SIX LECTURES will commence on FRIDAY, NOVEMBER 10th, at 5.30 o'clock.

Syllabus on application to the SECRETARY, University College, London, Gower Street, W.C.

Mr. J. G. LORRAIN, M.I.E.E., M.I.M.E., M.S.C.I.,

Fellow of the Chartered Institute of Patent Agents,

NORFOLK HOUSE, NORFOLK STREET, LONDON, W.C.

"PATENTEE'S HANDBOOK" Post Free on application.

THE CHEMICAL NEWS.

VOL. LXXX. No. 2083.

EVOLUTION OF CHEMISTRY IN THE LAST TWENTY YEARS.*

By DR. A. LADENBURG.

WHEN we look back upon the development of chemistry during the last fifteen or twenty years, we find that it is distinguished by the constantly increasing prominence of physical or, as many call it, general, chemistry, which from small beginnings has advanced to the position of a science of the first rank. Contributions to this end have, naturally, been made in particular by eminent scientists such as Horstmann, Gibbs, and van't Hoff, who have devoted themselves to this department exclusively, and, by their ideas and discoveries, have brought about its advancement. On the other hand, however, it cannot be denied that this advancement does not coincide fortuitously with the appearance of Ostwald's great Text-book of General Chemistry, but that the latter, in which the attempt is for the first time successfully made to give a complete representation of what has been accomplished up to the present in this department, aroused and stimulated the tendency towards investigation in an altogether exceptional manner. Further, the establishment by Ostwald and van't Hoff of the *Zeitschrift für Physikalische Chemie*, in which all the more important investigators in this department are active as collaborators, has done a great deal to advance the subject; so that this publication must be placed side by side with the best journals representing our science and be looked upon as of equal value with them.

In now passing on to the subject itself, I begin, in the first place, with the law of mass action, which is apparently destined to play a constantly increasing part.

These chemical studies received a new direction and a fresh stimulus from the theory of phases, due to Gibbs. The phase rule developed by him, and proved both by him and afterwards by van der Waals, is to the following effect:—Complete equilibrium can only exist when the number of phases present exceeds the number of components by one. By phases, are understood homogeneous portions of a system. Each state of aggregation represents at least one phase. In the solid or the liquid state two or more different phases may exist; a gas, however complex, can only form one phase. Complete equilibrium is a condition which depends *only* on the temperature, and is mostly definable by a certain value of the pressure. By components are understood all those chemical elements taking part in the equilibrium, whose quantities are subject to independent variation. Ammonium chloride, for example, has only one component, it being a matter of indifference whether we choose nitrogen, hydrogen, or chlorine. If excess of ammonia or of hydrochloric acid is added, there are then two independent components. Calcium carbonate, above its dissociation temperature, has two independent components, calcium and carbon; for the composition of the solid phases—calcium carbonate and calcium oxide—cannot be determined by the amount of calcium alone. Hence complete heterogeneous equilibrium is established in the case of ammonium chloride with two phases, and in the case of calcium carbonate with three phases.

If there are $n + 2$ phases and only n components, equilibrium is only possible at singular points; that is to say, at some definite temperature (multiple point, inver-

sion or transformation temperature). If there are just as many phases as there are components, the equilibrium is incomplete; that is, to each temperature there corresponds a series of pressures.

This phase rule has received numerous practical applications, the work of Roozeboom deserving especial mention. Roozeboom studied the connection of the states of aggregation, the equilibrium between water and sulphurous anhydride, the hydrates of ferric chloride, &c. The phase rule can also be applied to dissociation phenomena, to the reciprocal transformation of allotropic modifications of elements, and so forth.

More important perhaps than the phase rule (the significance of which is exaggerated by many, seeing that it merely furnishes a plan for the exposition of heterogeneous equilibrium) is van't Hoff's theory of solution. The conception that forms the foundation of this theory is based upon the well-known experiments of Pfeffer, which only became possible after the discovery by Traube of semi-permeable membranes.

In explaining osmotic pressure as the result of the impacts of the dissolved molecules upon the walls of the vessel, van't Hoff arrives at a comparison between substances in the dissolved condition and in the state of gas. The laws of Boyle, Mariotte, and of Henry Gay-Lussac, as well as the fundamental hypothesis of Avogadro, can now be applied directly to solutions; so that this branch, which has hitherto been one of the most obscure in the whole subject of chemistry, at once becomes fully accessible to investigation. As a consequence, important results, which are capable of being turned to account throughout the whole range of chemistry, are immediately obtained.

The important relations subsisting between the depression of freezing point, the diminution of vapour pressure, and the elevation of boiling point on the one hand, and the molecular weight of the dissolved substance on the other (which were ascertained experimentally and formulated by Raoult in particular), now attain their theoretical significance for the first time. As the outcome of this, and also in consequence of improvements and simplifications that Raoult's methods of molecular weight determination underwent, these methods very soon obtained a footing; and their results, especially those from the depression of the freezing point, are considered to be just as accurate as those from the vapour density.

Raoult had already pointed out, however, that aqueous solutions of salts of bases and of acids, in particular, did not agree with his rules; but always yielded results that were too low, and only attained to a value from one-half to one-third of that which had to be regarded as the normal number. All explanation of this anomaly was at first wanting, so that the general applicability of van't Hoff's theory appeared to be placed in doubt. The difficulty was got rid of in the same way as in the case of the abnormal vapour densities.

Arrhenius proceeded in this matter in exactly the same way that Cannizzaro, Kekulé, and Kopp had previously solved the other difficulty. His theory, advanced in 1887, adopts as actually existent that condition which must be assumed to exist in order to arrive at an agreement between the theory of van't Hoff and the numbers furnished by Raoult's rules. He draws attention to the fact that it is in the cases of solutions of those substances which are electrolytes and break up, under the influence of the electrical current, into their ions, that numbers are obtained which do not agree with theory. He now assumes that the ionisation does not merely take place as a result of the passage of the current, but that it occurs during the dissolution; and that the latter is thus accompanied by a more or less complete (electrolytic) dissociation, the extent of which depends principally upon the degree of dilution. A number of methods for determining the extent of this dissociation very soon presented themselves, as was pointed out by Arrhenius himself, but

* Read before the British Association (Section B), Dover Meeting, 1899.

also by Planck, Ostwald, and others; and (what is very important) these methods give results that agree with one another.

The hypothesis of Arrhenius found a great many opponents—indeed it could hardly have been expected that it would be otherwise. The assumption that an aqueous solution of common salt contains free sodium and chlorine ions (which, however, are nothing but electrically charged atoms that behave like free molecules) was certain to meet with opposition from chemists, since it stood in contradiction to observation and thus included something of a metaphysical nature. Besides, the explanation of many reactions that had formerly appeared simple was rendered much more difficult; as, for example, the decomposition of water by the alkali metals, since in this reaction no combination with oxygen and, on the other hand, no displacement of hydrogen ions by sodium ions, could be assumed. But of what consequence are considerations of this kind in face of the great advantages which the theory of electrolytic dissociation affords? A large number of otherwise inexplicable facts are satisfactorily explained by means of it. The so-called law of thermo-neutrality, of Hess, which has been confirmed, in part at least, by the well-known investigations of Thomsen and of Berthelot, is in complete accord with the theory of ionisation, and so are the exceptions to this law which must necessarily exist in cases of incomplete dissociation; whereas, without this theory the facts concerned constitute an incomprehensible puzzle.

It is similar with the identity of the heat of neutralisation of one and the same acid by means of different bases, and *vice versa*; also with the law of Oudemans and Landolt (in accordance with which the salts of optically active alkaloids and of optically active acids exhibit the same rotation in solutions of equivalent concentration), with the magnetic rotatory power, and with the atomic magnetism. Further, the principle in accordance with which the spectra of dilute solutions of different salts with similarly coloured ions are identical, and that according to which the molecular refractive power of the salts present in aqueous solution is an additive property, are explained in the same way. But probably the most important fact of this kind is that of the proportionality that exists between electrolytic conductivity and avidity in the case of acids, with which may be coupled the proof, furnished by Arrhenius, that the extent of the dissociation calculated from the electrolytic conductivity leads to very nearly the same results as that calculated from the depression of the freezing point. In these circumstances we cannot be in doubt as to whether the hypothesis of Arrhenius is warranted.

This ionisation theory, as it is now commonly called, leads us directly to electro-chemistry, which has undergone an advancement undreamt of twenty years ago, and has now developed into a separate branch of science that constantly leads to new scientific and practical results. The enthusiasm with which the discovery of the galvanic current and of the voltaic pile was welcomed, as sketched in Lecture V., was, as we now know, perfectly justified. And even although disillusionment followed the great discoveries of Ritter, Davy, Berzelius, and Faraday, and although this branch remained unfruitful for decades, still the opinion has been verified of those who believed that untold treasures lay here which should one day be disclosed.

The modern subject of electro-chemistry forms a continuation to those older discoveries, and to the important investigations of Hittorf and of Kohlrausch, which were now for the first time fully understood; and it leads to successive new discoveries.

In this connection, accumulators may first of all be mentioned here, since they have come into very general use, and without them it would scarcely be possible to employ electricity to advantage. Their introduction is the outcome of the discovery of polarisation by Ritter, and of the very exhaustive researches of Planté, which

extend as far back as the year 1859. Planté constructed very powerful examples of the so-called secondary batteries; and these were afterwards improved upon in important particulars by Faure.

The devising by Lippmann of the capillary electrometer, which depends upon the change in the surface tension of mercury produced by polarisation, is also worthy of mention.

The theory of the voltaic pile, for which we are indebted to Nernst, is very important. It is founded upon the theory of diffusion, which was advanced by Nernst himself, and upon the idea of solution tension deduced from van't Hoff's theory of solution. Nernst also developed the theory of concentration cells in the same way, and in doing so arrived at the same conclusions that Helmholtz had already reached by thermodynamical investigation.

These matters must, however, be disposed of here by merely alluding to them, since they really belong more to the domain of physics than to that of chemistry.

(To be continued).

ACTION OF ACETYL AND BENZOYL CHLORIDES ON DRIED COPPER SULPHATE (CuSO₄.H₂O).*

By W. R. HODGKINSON and Captain LEAHY, R.A.

THESE experiments were undertaken to ascertain whether there would be any ground for considering copper sulphate monohydrate as an acid body; the ratio of magnesium dissolved to copper deposited from a solution of copper sulphate (Clowes) suggesting such a nature.

Pure copper sulphate in fine powder was dried for a week at 98° C. An analysis showed that it contained exactly one molecule water. Weighed quantities of this salt were submitted to the action of acetyl chloride; firstly, by dissolving the chloride in metaxylene and agitating this with the fine powder of the copper salt and heating up to about 100° C. As this method was found to produce acetmetaxylene, CH₃CO.C₆H₃(CH₃)₂, it was abandoned.

Weighed quantities of the salt were then exposed in shallow platinum trays to the vapour of the chloride. After trying at several temperatures with varying results, it was found that an evident definite reaction took place when the vapour of the chloride was simply carried over the copper salt by a stream of well dried CO₂ at the ordinary temperature, 12–16° C. Under these circumstances the copper sulphate changed colour—from almost white to deep chocolate brown (copper sulphate monacetate)—and hydrogen chloride was evolved.

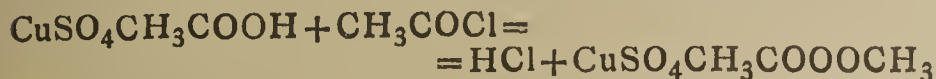
On heating the tube containing the tray with the salt to about 110° C., the compound evidently decomposed; it became quite white, acetic anhydride was given off, and the residue in the tray was pure CuSO₄. There was distinct evidence that at about 60–70° an intermediate compound was formed from the action of the excess of the chloride on the acetate first formed. This appeared to be a compound of the anhydride with the CuSO₄. Scarcely a trace of chlorine was retained by the copper salt.

Benzoylic chloride appeared to behave in a perfectly similar manner.

The figures obtained are not very close to theory, but scarcely leave any doubt about the composition of the products. In one experiment the copper salt absorbed 20.16 of acetyl. If the reaction proceeded according to CuSO₄.H₂O + CH₃COCl = HCl + CuSO₄CH₃COOH, the gain in weight would be 23.72 per cent. In another

* Read before the British Association (Section B), Dover Meeting, 1899.

experiment, 48.28 per cent acetic anhydride was combined. On the assumption that the reaction—



took place, the gain in weight should be 47.45 per cent. Similar results were obtained with benzoic chloride.

Ordnance College, Woolwich.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING SEPTEMBER 30TH, 1899.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, October 12th, 1899.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 208 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Sept. 1st to Sept. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 208 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during September was 2.38 inches, the thirty years average is 2.43 inches, making a deficiency of 0.05 inch; the total deficiency for the year is now 3.68 inches, or 19.9 per cent.

Our bacteriological examinations of 382 samples have given the results recorded in the following table; we have also examined 39 other samples, from special wells, stand-pipes, &c., making a total of 421 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	170
New River, filtered (mean of 76 samples) ..	4
Thames, unfiltered (mean of 26 samples) ..	574
Thames water, from the clear water wells of eight Thames-derived supplies (mean of 205 samples)	16
Ditto ditto highest	187
Ditto ditto lowest	1
River Lea, unfiltered (mean of 25 samples) ..	220
River Lea, from the East London Company's clear water well (mean of 25 samples) . . .	9

The waters of the Thames, Lea, and New River during September have been specially characterised by their extraordinary bacterial purity in the unfiltered state. Whereas in August the average microbic impurity of the Thames per c.c. was 2269, this month it is reduced to 574. The River Lea last month contained an average of 863 microbes, while this month it has been reduced to 220. The New River last month contained 410, and this month it has sunk to 170.

The raw water being so much better, the filtered water is of higher quality than usual. The purification by storage and regulated filtration has become so effective

that, as we have pointed out again and again, the quality of the distributed water now is practically independent of variations in the microbic impurities that occur during the course of the year in the respective sources of supply.

When storage and filtration are effectively conducted, water is produced for distribution containing an average of less than 100 microbes per c.c. Such a result is regarded by the highest authorities as eminently satisfactory, and such a water has never been known to cause a water-borne disease. It will be noted in many of our reports and on many occasions that the clear-water wells of the London Companies contain far less than 100 microbes per c.c. It is true that some individual filter may become temporarily defective, such as, for instance, in the case of the Thames-derived sample this month, which gave 187 microbes per c.c.; but this is immediately detected and remedied within a short period of time, so that next day the microbial impurity of the water is almost invariably reduced below the recognised standard of 100. Owing to the large number of samples bacteriologically examined every month (amounting in September to 421), it is easy to ascertain and remedy at once any defective filter.

Taken as a whole, the quality of the London water supply has rarely, if ever, been so good as during the course of last month, and for any person, professing to be conversant with the question of water supply, to talk at the present day of the drinking water of London as a "limited supply of diluted sewage, in the place of fresh water," is to indulge in a misrepresentation of facts which cannot be too strongly condemned.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

JAMES DEWAR.

LIQUID AIR AS AN ANALYTIC AGENT.*

By Professor DEWAR, M.A., LL.D., F.R.S.

(Concluded from p. 190).

Thermal Transparency at Low Temperatures.

PICTET, after an elaborate investigation, concluded that below a certain temperature all substances had practically the same thermal transparency, and that a non-conducting body became ineffective at low temperatures in shielding a vessel from the influx of heat. Experiments, about to be detailed, however, prove that such is not the case, the transference of heat observed by Pictet appearing to be due not so much to the materials themselves as to the air contained in their interstices. Good exhaustion in the ordinary vacuum vessels used in low temperature work reduces the influx of heat to one-fifth of what is conveyed when the annular space of such double-walled vessels is filled with air. If the interior walls are silvered, or excess of mercury is allowed to remain, the influx of heat is diminished to one-sixth of the amount entering without the metallic coating. The total effect due to the high vacuum and silvering is to reduce the ingoing heat to one-thirtieth of the original amount, *i.e.*, roughly, to 3½ per cent.

By filling the annular space between the walls of several similar vacuum vessels with various substances, and exhausting them all to the same low pressure, large differences in the thermal isolation were observed. The rate of evaporation of equal volumes of liquid air contained in the respective vessels measures the rate of influx of heat. Moreover, it appears that what might be called under the circumstances the thermal transparency of some materials diminished at very low temperatures instead of increasing, as had been asserted. Thus, of two

* A Lecture delivered before the Royal Institution of Great Britain, April 1, 1898.

vacuum tubes (one simply exhausted, and the other having powdered carbon in the vacuum space), the latter, at low temperature, was the most efficient preserver of liquid air, showing that the carbon diminished the radiation and gas convection. But when the vacuum was destroyed and air admitted into the space, the liquid air in the carbon tube boiled off much more vigorously than that in the simple tube, indicating that at ordinary temperatures carbon allowed more heat to pass than did air.

In conducting these experiments, generally sets of three double-walled glass tubes, as nearly identical in size and shape as possible, were mounted on a common stem, and two out of the three filled with different kinds of powders, while the third is left empty as a standard

outer surface of the vacuum tubes being maintained at a steady temperature by immersion in a large vessel of water. Neither the tubes nor the shape of the vacuum space in each were absolutely identical, so that the results are simply comparative. The general ratio of heat propagation found for two substances when different sets of double-walled tubes of about the same form and proportion were compared, remained substantially constant when a high vacuum was reached. A confirmation of the results was generally made by noting the time required to evaporate the whole of the air from each tube. The annular vacuum space had generally a thickness of 4 to 5 m.m., and was in each case completely filled up with the solid. In reality, however, the absolute fraction of the

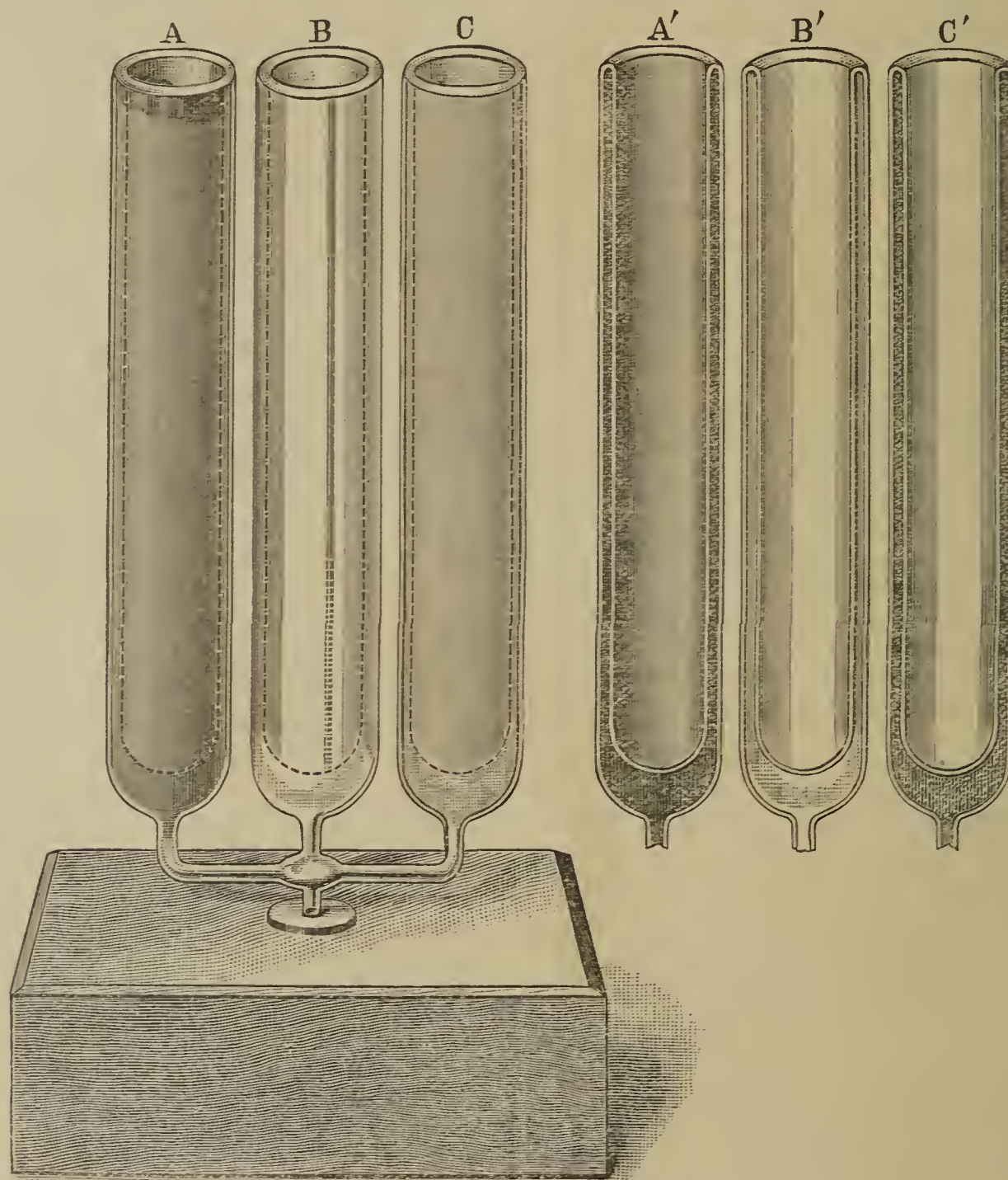


FIG. 3.—Three Tubes blown on to one Stem, so that the Exhaustion in each would be identical.

A, Filled with lampblack between the inner and outer tubes. B, Annular space left empty. C, Filled with silica between the tubes.
A', B', C', The same tubes in section.

for comparison (Fig. 3). In this way each set had the same vacuum, and, as intercommunication between the tubes after sealing off from the pump was left free, any deterioration in the vacuum on keeping affected all three vacuum tubes to the same extent.

The preparation of such tubes entails enormous labour, because it takes days of exhaustion with a mercurial pump to extract the occluded gases, even at as high a temperature as the glass would stand. Before beginning the experiment, the vacuum tubes of each triple set were filled with liquid air, and allowed to stand half an hour in order to get the heat conduction in the porous mass into a steady state. The tubes after this treatment were filled to the same height, and the relative times required to distil off the same volume of liquid air from each observed, the

space filled by the solid did not exceed one-half. The effect of any considerable inequality in the thickness of the non-conducting powders was ascertained by comparing two vacuum tubes, one having double the thickness of vacuum space of the other, and each then filled with precipitated silica. Taking the unfilled vacuum tube as the unit for comparison described above, then the single thickness of silica increased the insulation to 6 and the double thickness to 8. The following table contains the results of a number of experiments with triple sets of double-walled tubes filled with different substances, when exhausted and unexhausted. The results are expressed in the relative times required to volatilise the same small volume of liquid air from each tube. This is most readily done, after filling each tube with the same volume of

liquid air by noting the time required to fill a given vessel standing over the pneumatic trough with the gaseous air distilling off.

In each triple set the unit taken for comparison is the time value of the free vacuum spaced tube.

			Vacuum.	Atmospheric pressure.
Empty tube	1	1.0
Charcoal	5	0.7
Magnesia	2	0.6

			Vacuum.	Air.
Empty tube	1	1.0
Lamp-black	5	0.7
Silica	4	0.7

					Vacuum.
Empty tube	1
Phosphorus (amorphous)	1
Mercuric iodide	1.5

Empty tube	1
Lead oxide	2
Bismuth oxide	6

From these experiments it will be seen that silica charcoal, lamp-black, and oxide of bismuth, all increase the insulation to 4, 5, and 6 times that of the empty vacuum space. In tubes generally which did not reach such a high vacuum the relative insulating effect of these powders could be raised as much as 1 to 8 or 1 to 10. In this case the influx of heat per unit of time in the vacuum

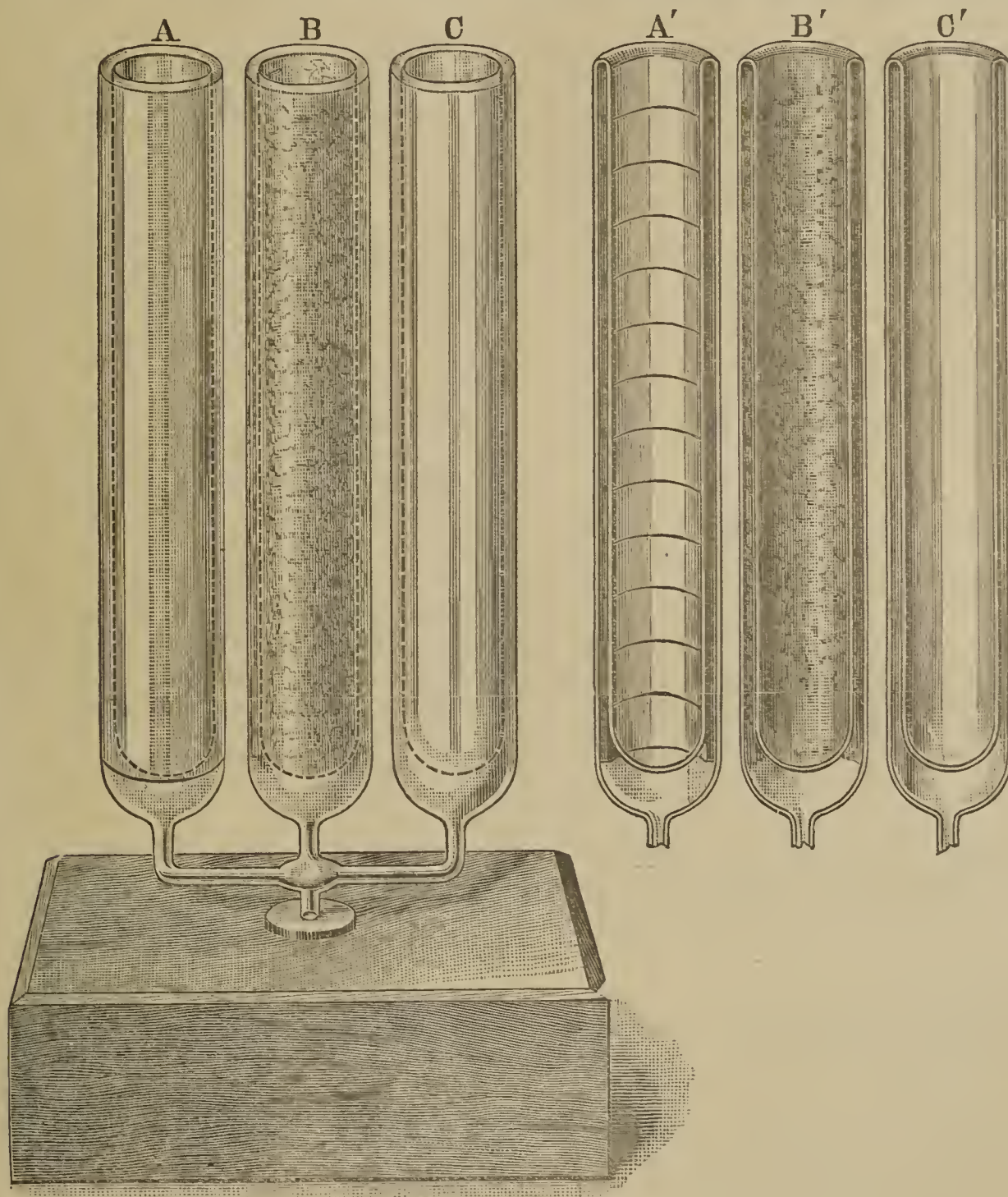


FIG. 4.—Three Tubes blown on to one Stem, similar to Fig. 3.

A, Vacuum space having three turns of gold paper, gold outside. B, Vacuum space having some pieces of gold leaf put in so as to make contact between walls of vacuum tube. C, Vacuum space empty. A', B', C', The same tubes in section.

						Vacuum.
Empty tube	1
Graphite	1.3
Alumina	3.3

Empty tube	1
Lamp-black	4
Lycopodium	2.5

Empty tube	1
Calcium carbonate	2.5
„ fluoride	1.25

Empty tube	1
Barium carbonate	1.3
Calcium phosphate	2.7

tube which did not contain any finely divided powder was necessarily much greater. As the chief communication of heat is by molecular bombardment, the fine powders must shorten the free path of the gaseous molecules, and the slow conduction of heat through the porous mass must make the conveyance of heat energy more difficult than when the gas molecules could directly impinge upon the outer glass surface maintained at a higher temperature. To separate the true conduction from the radiation and the gas motion would require far more elaborate experiments, but these are sufficient to prove that the presence of certain finely divided solids in the high vacuum space of the vessels used in low temperature research improves the heat insulation, while in the presence of air the same bodies facilitate the transference of heat. This is the explanation of Pictet's apparently extraordinary results.

In no case was the diminution of the influx of heat, in the case of the use of finely divided solids, ever so effective as a high vacuum, in an empty tube, the glass surfaces being silvered. This is seen by reference to results recorded in Tables Nos. 1, 2, and 3, where the insulation is increased in the proportion of more than 1 to 7, which is decidedly better than anything reached by the use of powders.

It will be noted that the use of silica and charcoal to fill up the annular spaces between the walls of these silver-coated vacuum vessels has produced very different results from those recorded in the former experiments with plane glass surfaces. Instead of the heat insulation being increased from 4 to 5 times by the use of such powders, it is now only very slightly benefited. This suggests that the finely divided solid affects chiefly the combined radiation and conduction factors.

A further set of experiments was made with similar vacuum tubes, replacing the powders by metallic and other septa (Fig. 4). Various papers coated with metallic powders in imitation of gold and silver which are in common use, were compared with black paper and a comparison made between the use of sheet lead and aluminium, all under similar conditions.

The following tables express the comparative results of the different experiments:—

(1).				
Vacuum space empty, not silvered	1	
Same space unexhausted	0.25	
Vacuum space empty, silvered on both surfaces	7.4	
(2).				
Vacuum space empty, silvered on inside surfaces	1	
Silica in silvered vacuum space	1.1	
(3).				
Empty silvered vacuum	1	
Charcoal in silvered vacuum	1.25	
Vacuum space unsilvered	1	
„ silvered inside	5	
„ in annular space with glass test-tube silvered	6	
(4).				
Vacuum space empty	1	
Three turns silver paper, bright surface inside	4	
Three turns silver paper, bright surface outside	4	
(5).				
Vacuum space empty	1	
Three turns black paper, black outside	3	
Three turns black paper, black inside	3	
(6).				
Vacuum space empty	1	
Three turns gold paper, gold outside	4	
Some pieces of gold leaf, put in so as to make contact between walls of vacuum tube	0.3	
(7).				
Vacuum space empty	1	
Three turns, not touching, of sheet lead	4	
Three turns, not touching, of sheet aluminium	4	

The experiments show that liquid air can be conveniently used to study many important problems of heat transmission.

(To be continued).

On Hæmatine from Blood, and its Variations according to the Animal Species.—P. Cazeneuve and P. Breteau.—The authors give the results of their analyses of hæmatine from bullock, horse, and sheep's blood; they include the C, H, N, Fe, and O. They found the proportion of N to Fe to be 4.1 : 1 with bullock, 4.3 : 1 with horse, and 3.5 : 1 with sheep.—*Bull. Soc. Chim.*, xxi., No. 8.

VARIATIONS IN SEA-WATER, WITH THE DEPTH, PARTICULARLY WITH REGARD TO THEIR IODISED COMPOUNDS.

By A. GAUTIER.

WATER taken from the surface of the Atlantic does not contain a trace of iodides or iodates (*Bull. Soc. Chim.*, Series 3, xxi., 566). The whole of the iodine is found in the form of matter of a very complex nature,* and this element does not become apparent until after fusing the residue from the water with potash. In water taken at the entrance to the Channel, at 40 kilometres from the shore, I found:—

Iodine per Litre of Water.

Mineral iodine	M.grms.
Iodine removed by the porcelain filter	0.000
(organisms, &c.)	0.520
Latent iodine of the soluble compounds	1.820
Total per litre	2.320

I have just made similar observations with Mediterranean waters taken at the surface, 11 kilometres from the shore opposite Monaco, and I found:—

Iodine per Litre of Water.

Mineral iodine	M.grms.
Iodine removed by the porcelain filter	0.000
(organisms, &c.)	0.286
Iodine from the soluble complex compounds	1.960
Total per litre	2.241

These results prove that:—1. Sea-water taken at the surface, in two seas far apart from each other, contain almost the same total iodine, it being understood that the samples are taken far from the mouths of rivers and after continued fine weather. 2. In the waters of the Mediterranean, as well as in that of the ocean, there is no trace of iodides or iodates to be found if the samples are taken at or within a few metres of the surface. 3. In sea-water the iodine is contained at the surface, partly in the insoluble and organised state and partly in the soluble state; in this case it forms part of complex compounds partially or totally organic, nitrated, phosphorised, and dialysable.

The nature of these soluble iodised compounds merits a much closer study, but it is not without difficulties; the iodised matter disappears from the sea-water when it is concentrated. Water which I collected in salt-marshes evaporated spontaneously in the air, and, showing 24° B., did not contain the least trace of mineral or organic iodine. A small quantity of phosphates still remain, but the lime was entirely precipitated, probably carrying with it the iodised material.

Whatever may be the nature of this complex iodised substance, my opinion is that, coming from the depths of the sea, and contained originally in the primitive rocks, then in the water in the mineral form, the iodine, when it arrives in those regions of the sea rich in living organisms capable of assimilating it, passes partially or totally into the organic state. This phenomenon, which thus causes the disappearance of the mineral iodine, should be at its maximum in that portion of the sea which is penetrated by light, and should diminish—without, perhaps, entirely disappearing—in the lower regions of the sea which are plunged in absolute darkness. If things do happen in this manner, we may hope to find, at depths of from 400 to 500 metres, and lower, where algæ no longer exist

* These compounds are entirely or partly organic, but I have not yet decided the point as to whether calcareous iodosulphates or iodo-phosphates, mixed or feebly united, are found.

and only a few rare living organisms are found, iodine in its primitive form—that is to say, mineral.

To submit this theory to the test of experiment, I first had recourse to the waters of the Mediterranean, the temperature of which is almost invariable (about 13°), and where it has been found that below a depth of 300 metres there is complete repose, so that the different layers of water are not mixed by any currents. For the purpose of collecting samples I am indebted to the great kindness of His Highness the Prince of Monaco, whose zeal for everything connected with oceanography is well known. By his help I was enabled to take samples of water at different depths. These were taken on the 10th of May last, after continued fine weather, at 11 kilometres from the shore opposite Monaco. Four samples of 2 litres each were taken in the same vertical line,—the first at 0.5 metre below the surface, the second at 780 metres, the third at 880 metres, and the last at 980 metres in depth, where the bottom, formed of a reddish sandy clay, was touched. For the purpose of noticing, first of all, the influence which the living organisms inhabiting it might have on the water, and particularly on its iodised compounds, it was necessary to measure their mass, and even to determine the nature of those which might also be found below the region near the surface. For this purpose the 2 litres of water taken at 780 metres were immediately treated with 1/50th of formol, a substance which immediately fixes the plasmas and living matters in the state in which they are found, and which thus allows them to be collected and examined under the microscope for the purpose of observing the state in which they exist at the moment of this species of embalming. The waters from 780 metres thus formolised were allowed to stand for twelve days to deposit all matters in suspension, and then carefully syphoned off, and the bottom layer with the deposit was run into a glass tube 1 metre long, drawn out and closed at the end. This was left for ten days longer; the deposit was then collected at the bottom by centrifugal force without having undergone any filtration. In 2 litres only 1/15th of a m.grm. was found; this was examined under the microscope, but did not contain any living algæ; it consisted principally of mineral (quartz) splinters or flakes, yellow and brown scales with an articulated appearance, formless masses having the appearance of protoplasm become granular, oily, and discoloured, and a few sponge spiculæ; there were also found three or four siliceous envelopes of diatoms, a foraminifera shell, a few bacteria; finally a small copepod, living at the moment of capture, and, according to its volume, weighing about 0.15 m.grm. In a word, at a depth of 780 metres, with the exception of this little crustacean, no other living organisms were found besides a few very rare protozoa and bacteria, representing a proportion of 1/10th at the most of the accompanying *débris*, and which themselves had a total weight of not more than 1/30th of a m.grm. per litre of water.

The total absence of microscopic algæ and the very small mass of the other living organisms thus established at this level, and *a fortiori* at lower levels, it became interesting to find what influence the disappearance of these organisms had on the composition of sea-water, especially with regard to the variation of the iodised compounds. We therefore examined comparatively the samples taken at the surface, at 880 metres, and at 980 metres; these samples were taken in ground-glass stoppered bottles, and kept in the dark until they were analysed. These waters were examined for their density; their total solids; their total chlorine, bromine, and iodine; their richness in iodine, and the nature of their iodine compounds.

Density at Different Depths.—This was taken at 4° and on 250 c.c. at a time, for greater accuracy; we found:—

	Density.	Weight of 1 litre at 4°.
Surface.. ..	1.03014	1030.14 grms.
880 metres	1.03104	1031.04 „
980 „	1.03076	1030.76 „

The density of the water at the bottom is, as we see, slightly less than that of the water taken 100 metres higher up. The small difference is only 0.28 gm. less in a litre; this is confirmed, as will be seen, by the weight of the dry residue, as well as by other estimations. It is probable that the sea receives, especially at points near high mountains, as is here the case, fresh water from deep springs, which slightly diminish the density of the water at the bottom, and which only mixes very slowly by diffusion with the sea-water, which is here quite at rest.

Dry Residue.—This was taken on 10 c.c. of water measured at 4°; to it was added 0.02 of dry carbonate of soda, to prevent loss by dissociation on heating; we then deduct the weight of the salt added; complete desiccation was effected at 105° until the weight was constant; we found:—

Dry residue per litre at 4°.

Surface	43.40 m.grms.
880 metres	44.78 „
980 „	43.41 „

These weights are very high: the weight of salts per litre is from 35 to 38 grms. in the Atlantic; Laurent found 40.7 grms. per litre in the Mediterranean, near Marseilles; but our three weights agree among themselves.

Chlorine—Bromine—Iodine.—The total weight of these three elements was:—

	Chlorobromiodide of Ag per litre at 4°.	Corresponding theoretical amount of NaCl.
Surface	0.8579 m.grm.	34.92 m.grms.
880 metres	0.8844 „	35.99 „
980 „	0.8767 „	35.68 „

The sea-salt thus calculated is certainly too high, the alkaline-earthly chlorides being here transformed by the calculation into chloride of sodium. But we still notice that the principal salts are more abundant at a depth of 880 metres than at 100 metres lower down.

Iodised Compounds.—The water examined from this point of view, three days after the sample was taken, had not been exposed to light for an instant; it was necessary, in fact, to prevent the modifications which the living organisms might undergo under its influence, particularly with regard to the iodised compounds. The matter in suspension, living or not, was separated by filtration through porcelain in the dark. The iodine was then estimated in its three forms, as has been already described in a previous paper. We found:—

Iodine per Litre (Surface).

	M.grms.
Iodine removed by the filter (living organisms, insoluble bodies, &c.)	0.286
Iodine entirely or partially organic, in the soluble state	1.960
Mineral iodine (iodides, iodates, &c.)	0.000
Total	2.246

Iodine per Litre (880 Metres).

Iodine removed by the filter (organic matter, &c.)	0.100
Iodine entirely or partially organic, in the soluble state	2.130
Mineral iodine (iodides, &c.)	0.150
Total	2.380

Iodine per Litre (980 Metres).

Iodine removed by the filter (organic matter, &c.)	0.065
Iodine entirely or partially organic, in the soluble state	1.890
Mineral iodine (iodides, &c.)	0.305
Total	2.260

The examination of these figures leads to the following conclusions:—1. The total iodine of the waters of the Mediterranean is practically constant from the surface to the bottom of the sea; the intermediate layer at 880 metres always contains a slightly greater proportion. 2. The water of the Mediterranean appears, on the surface, to contain slightly less total iodine (2.25 m.grms.) than that of the open sea (2.40 m.grms.) per litre. 3. As the living organisms, algæ or protozoa, increase in the water, the mineral iodine as iodides and iodates diminishes—from 0.305 m.grm. per litre at the bottom, it becomes 0.150 m.grm. at 100 metres above, and it has totally disappeared at the surface, and probably long before that point. This result confirms the preconceived ideas which have guided us in this research. 4. On the contrary, as the organic iodine diminishes the organised iodine increases as we leave the bottom, and at the same time as the mass of living organisms which fixes this element increases. 5. The totally or partially organised iodine—that is, the iodine in the soluble state forming part of the matter which goes through the filter—does not sensibly vary, although in the case of the Mediterranean it appears to have a slight maximum at about 880 metres. The substance from which this iodine is derived does not seem necessarily to belong to the living organisms—so numerous at the surface, and so rare, as we have seen, from 400 metres downwards.

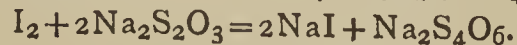
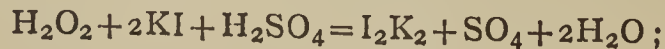
It is altogether remarkable to observe the existence at all levels in the Mediterranean, as in the open sea, of this totally or partially soluble organic matter, as well as of the glutinous material retained by the filter. These two substances, both very rich in iodine and very complex, were found in every case, although they are a little less abundant at the greatest depths; they merit a special study to themselves.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 16.

COMPARATIVE ACCURACY OF TITRIMETRIC AND GASOMETRIC METHODS OF ESTIMATING HYDROGEN DIOXIDE IN PRESENCE OF VARIOUS PRESERVATIVE AGENTS.*

By CARL E. SMITH.

(Concluded from p. 195).

Titrimetric Thiosulphate Method.—This was first recommended by C. T. Kingzett (*Journ. Chem. Soc.*, 1880, vol. xxxvii., p. 802), and later by H. Thoms (*Arch. Pharm.*, 1887, vol. xxxv., pp. 335—343). It is based on the fact that hydrogen dioxide liberates a definite quantity of iodine from iodides in acid solution, the iodine being titrated with sodium thiosulphate in the usual manner.



Thoms proceeds by warming 0.5 grm. of potassium iodide, 1 grm. of 20 per cent sulphuric acid, and 50 c.c. of water to 40° C., adding 0.5 c.c. of the hydrogen dioxide solution, shaking about five minutes, and titrating the liberated iodine with N/10 thiosulphate, then warming again to 40°, again titrating the appearing iodine, and repeating until no further liberation of iodine takes place. Carried out in this way the method is rather slow and tedious, requiring at least fifteen minutes for completion; but, since it was stated to be accurate, the writer decided to include it in his experiments, and found later, that by omitting the greater part of the water, so as to reduce the bulk of the solution to about 15 c.c. for the above-mentioned quantities, heating might be dispensed with,

and the reaction would nevertheless be ended within five minutes. The final result was found to be the same, whether working with dilute or with concentrated solutions. One possible source of error with the latter is that, when standing in a very warm room prior to titration, slight losses of iodine might occur through vaporisation. This could, of course, be readily seen and proper precautions taken to prevent loss. The following mode of operation is considered the most practical:—Dilute the solution to be tested to exactly ten times its volume with distilled water, measure 5.6 c.c. of the dilution (=0.56 c.c. of sample) into a beaker or flask, add 5 c.c. of 10 per cent sulphuric acid and 5 c.c. of a 10 per cent solution of potassium iodide, and let the mixture stand for five minutes. Then gradually add N/10 thiosulphate, with constant agitation, until the colour of the solution is discharged. If the solution remains colourless upon standing a few minutes longer, the titration is finished. If a colour should appear, add sufficient thiosulphate solution to remove it. The total number of cubic centimetres of the thiosulphate solution required indicates the number of volumes of available oxygen the sample contains. If it is considerably stronger than ten volumes, the result will probably be too low, unless more time is allowed for the reaction. In such a case correspondingly more potassium iodide and sulphuric acid should be taken. No starch paste is necessary, as the end-reaction is sufficiently sharp without it, particularly when the solution is placed over a white surface. In cases in which an accurate dilution of the sample is impracticable, 1 c.c. of the undiluted sample may be taken, with double the quantities of reagents given above. The number of cubic centimetres of N/10 thiosulphate required must then be multiplied by 0.56 to obtain the strength in available oxygen. Or, instead of N/10 thiosulphate (24.8 grms. of crystallised salt per litre), a solution containing 44.29 grms. per litre may be used. In the latter case each cubic centimetre consumed indicates one volume of available oxygen, provided 1 c.c. of sample has been taken. The per cent of hydrogen dioxide is obtained by multiplying the volume strength by 0.3038. (This is not strictly correct, as the specific gravity of the solution is left out of consideration). It is important that the reagents used are free from such impurities as would act as reducing or oxidising agents. The sulphuric acid should be free from sulphurous, arsenious, and nitric acids, and the potassium iodide from iodate. Sodium thiosulphate (commercially called "hyposulphite of soda") is very frequently found in the market of a sufficiently high degree of purity to make it permissible to prepare the N/10 solution for the assay of hydrogen dioxide, by dissolving exactly 24.8 grms. of it in enough distilled water to make 1 litre, instead of standardising it with iodine. It should be in colourless, transparent, uneffloresced crystals, and contain no chloride or sulphate, or at most only traces of sulphate. The crystals should be coarsely powdered, and any interstitial mother-liquor removed by pressing between folds of bibulous paper before weighing. The writer, however, prefers to re-crystallise the commercial salt, and finds the solution prepared from this, in the manner indicated above, fully as accurate as when standardised with pure iodine.

This method has been treated of more at length than the others, because it proved to be the best of those examined, as will be explained more fully below.

Comparison of Methods on Commercial Samples.—A few commercial solutions of hydrogen dioxide of varying strength and purity were examined with the object of gaining some knowledge of the comparative accuracy of the four methods described. The pharmacopœial tests were also applied, and the results embodied in Table I.

No barium salts or fluorides were detected by the U.S.P. tests. The limit of acid (0.5 c.c. of N/1 soda for 50 c.c.) was exceeded in three samples. The limit of residue (0.25 grm. for 50 c.c.) was exceeded in one. Nos. I., II., and III. are aqueous solutions, stated to contain respectively 10, 15, and 30 volumes of available oxygen,

* Report from Research Committee D, Section II., of the Committee of Revision of the U.S. Pharmacopœia. From the *American Journal of Pharmacy*.

TABLE I.

	Sample I.	Sample II.	Sample III.	Sample IV.
Strength by KMnO_4 (titrimetric) method.. ..	10.3, 10.35 vol.	15.45, 15.45 vol.	29.45, 29.35 vol.	26.65, 26.65 p.c.
Strength by KMnO_4 (gasometric) method.. ..	10.6, 10.3, 10.1, 10.4 vol.	15.5, 15.35 vol.	30.15, 31.6 vol.	27.85, 26.75 p.c.
Strength by $\text{Ca}(\text{ClO})_2$ method	10.45, 10.4 vol.	15.5, 15.55 vol.	29.7, 29.9 vol.	26.95, 27.2, 27.1 p.c.
Strength by $\text{Na}_2\text{S}_2\text{O}_3$ method	10.3, 10.35 vol.	15.5, 15.55 vol.	29.4, 29.4 vol.	26.2, 26.4 p.c.
Acidity in c.c. of N/1 soda required for 50 c.c.	1.85 c.c.	0.95 c.c.	2.1 c.c.	Neutral
Residue from 50 c.c. at 100°C.	0.339 grm.	0.029 grm.	0.124 grm.	0.015 grm. from one tube (3.025 grm.).
Impurities found	HCl, NaCl, H_3PO_4	HCl, H_3PO_4	HCl, H_2SO_4 , H_3PO_4	Not identified

TABLE II.

Substances added.	Permanganate method (titrimetric).	Hypochlorite method.	Thiosulphate method.
Glycerin, 5 per cent	10.55, 10.45	10.2, 10.25	10.25, 10.25
Boroglycerin, 5 per cent ..	10.45, 10.5	10.15, 10.05	10.25, 10.3
Boric acid, 5 per cent.. ..	10.3, 10.25	10.3, 10.2	10.3, 10.25
Boric acid, 20 per cent ..	10.3, 10.3	10.1, 10.15	10.3, 10.35
Salicylic acid, 0.2 per cent..	11.3, 11.5	9.6, 9.7	10.3, 10.3
Salicylic acid, 2 per cent ..	15.0	9.55, 9.4	10.3, 10.4
Benzoic acid, 0.2 per cent..	10.45, 10.4	10.15, 10.15	10.45, 10.4
Salol, saturated solution* ..	10.25, 10.25	10.0, 9.85	10.2, 10.2
Acetanilide, 0.5 per cent ..	10.3, 10.3	10.1, 10.2	10.25, 10.25
Ether, 10 per cent	10.35, 10.35	10.65, 10.7	10.25, 10.25

* Prepared by diluting 13.35 c.c. of H_2O_2 solution with a cold, aqueous, saturated solution of salol to 100 c.c.

TABLE III.

Grms. of glycerin added to 1 c.c. of solution.	Permanganate method (titrimetric).	Permanganate method (gasometric).	Hypochlorite method.	Thiosulphate method.
0.5	10.8			
1	11.25, 11.2	9.95, 9.8	10.5, 10.55	10.3, 10.3
2	12.25		10.5, 10.4	10.35

while No. IV. is an ethereal solution claimed to contain 25 per cent of hydrogen dioxide. These claims as to strength are reasonably well supported by the results obtained. It will be seen that with some samples the results by the different methods vary more than with others, the differences being greatest in the case of Sample IV. Subsequent experiments showed the discrepancies in this case to be at least partially due to the presence of ether, and the fourth method to be the most trustworthy for the assay of ethereal solutions. The first, third, and fourth methods are fairly well in accord with each other, but the second frequently gave figures differing not only from those obtained by other methods, but also differing widely among themselves in duplicate estimations. This method, because of its seeming unreliability, was left out of consideration in later experiments.

Estimation in presence of Preservative Agents.—In the experiments to be described, Sample II. was used, as it proved to be the purest of the aqueous solutions at the writer's disposal. The mixtures were prepared by diluting 13.35 c.c. of this solution, containing 15.45 volumes of available oxygen, to 100 c.c. with distilled water, after adding a definite quantity of the substance whose influence on the methods was to be determined. Five c.c. of the dilution represent 1 c.c. of a solution of two-thirds the above strength, or 10.3 volumes. It was thought best to base the calculations on this latter standard of strength, as being the more customary one. The percentages given in Table II., of preservative substances added, were also based on this standard. In some cases these were added in the quantity that would be required to make a saturated solution in the amount of 10 volume solution present; in other cases, much larger quantities were taken. The results are given in volumes of available oxygen.

These results show that the accuracy of the titrimetric permanganate method is affected slightly by the presence of moderate quantities of glycerin or boroglycerin, but that in the presence of the quantities that would be added to the solutions by manufacturers, which would

hardly exceed 1 per cent, the difference in result would not be noticeable. In presence of salicylic acid, however, the method is worthless. There is evidence, also, that ether is not entirely without influence. It may be stated, then, as a generalisation, that in presence of organic substances, titration with potassium permanganate cannot be depended upon to always give sufficiently accurate results for pharmacopœial purposes.

With the hypochlorite method there is a tendency toward low results, most marked in presence of salicylic acid. The presence of ether introduces an error, which is probably due largely to the increased vapour tension. While the inaccuracies of some of the results of this method may be partially attributed to a neglect to make corrections for variation in barometric pressure and for the tension of water-vapour, it was proven by parallel estimations during the same atmospheric pressure, that some of the added substances without doubt exert an influence on the volume of gas liberated. This method, then, is also unreliable in presence of organic matter, but less so than the permanganate methods.

The accuracy of the thiosulphate method is practically unaffected by the addition of any of the substances given in Table II. The differences in the results are probably due as much to variation in measuring, &c., as to any other cause, and it would seem that, under such conditions as are at all likely to occur in practice, the method can be depended upon to give very serviceable results.

Estimation in presence of Larger Quantities of Glycerin.—In view of the fact that hydrogen dioxide is sometimes used medicinally in combination with glycerin, and that assays of such mixtures, containing comparatively large proportions of glycerin, may become necessary, trials were made to determine the comparative accuracy of the several methods under such conditions. A 10.3 volume solution was used, and the results are stated in volume strength (Table III.).

It is seen that the thiosulphate method is first and the hypochlorite second in point of accuracy, while the two

others are worthless. With permanganate the reaction is at first extremely slow, but it gradually quickens and the permanganate is decolorised as rapidly as it is added until near the end, when it again becomes very slow.

Summary.—The titrimetric permanganate method is accurate and reliable for the valuation of solutions containing only mineral acids and their alkali salts as impurities. With solutions containing glycerin or boroglycerin in quantities below 5 per cent the results are but slightly raised; in presence of larger amounts the method is inapplicable. Ethereal solutions give results a little too high. Salicylic acid interferes seriously, even in small quantity. The use of this method should be avoided whenever organic matters are suspected to be present. Applied gasometrically, the permanganate method is unreliable in all cases.

The hypochlorite method gives serviceable results in absence of preservatives. In their presence they are liable to fall too low, and with ethereal solutions they are too high.

The thiosulphate method is simple, rapid, and accurate, and its accuracy is not lessened by the presence of the usual preservative agents, nor by large quantities of glycerin. It is applicable in all cases, so far as known. It can be said of gasometric determinations in general, that they require more time, attention, and apparatus than titration methods, and that the results obtained by them cannot be expected to approach the latter in accuracy, unless suitable corrections, requiring tedious calculations, are made for variation in temperature and atmospheric pressure at least.

THE DEFINITION OF THE ELEMENT.*

By F. P. VENABLE.

IT is with hesitation that I enter upon so speculative a discussion as the nature of the elements, and yet there are reasons why it should prove of great profit to draw the attention of this representative gathering of the chemists of America to this subject. We have nearly reached the close of the first century in which these elements have been the subject of experimental research. The ingenuity and the patient labour of an army of workers have been directed at the solution of the many problems connected with these elementary substances, and the ultimate aim, the goal, of all their striving has been the discovery of the properties and the nature of the atom.

It is eminently fitting that, as we stand at the threshold of the new century, we glance back along the road we have already come and take some account of the progress we have made. The quicksands of mere speculation must be avoided, and yet the mental vision, the "scientific imagination," must be called into service in considering that which so far transcends our cruder actual vision as the incomparable atom itself. There is another reason for considering the nature of the elements. At several times during the century a wider vision has made it necessary to recast the definition of the elements to accord with increasing knowledge. It would seem as if another such period of change were approaching. There may be need of a truer definition, and how shall this be realised or the new definition properly fitted unless the knowledge gained be summed up and appreciated?

The conception of an element among the Greek philosophers and the earlier alchemists was very different from the modern idea. This conception sprang from the theories as to the formation of the material universe. The elements were the primal forms of matter seen only combined, impure, imperfect. They were the essences or principles out of which all things were evolved. In the

four-element theory, which was so widely spread among the ancients, the fire, air, earth, and water were not the ordinary substances known under these names, but the pure essences bestowing upon fire and water their peculiar properties. These essences were not thought of as actual substances capable of a separate material existence, and gradually the belief that a transmutation was possible between them sprang up. Thus they themselves might be derived from some one of them, as fire or water. The Thalesian theory, deriving all things from water, was especially popular, and was not completely overthrown until the modern era.

When, later on, the alchemist conceived of all metals as composed of sulphur and mercury, it was an essence or spirit of mercury that was meant. Certain common characteristics—as lustre, malleability, fusibility, combustibility, &c.—naturally led them to think of the metals as belonging to the same order of substances containing the same principles, the relative proportions and purity of which determined the variations in the observed properties. Thus the properties of the metals depended upon the purity of the mercury and sulphur in them, the quantities of them, and their degree of fixation. The more easily a metal was oxidised on being heated, the more sulphur it contained, and this sulphur also determined its changeability. The more malleable it was, the more mercury entered into its composition. If only something could be found which would remove the grossness from these essences, some unchanging, all-powerful essence, which, because of their search for it, gradually became known as the "philosopher's stone," then the baser metals might be transmuted into the noble gold when the sulphur and mercury were perfectly balanced and free from all distempers.

As has been said, these principles entering, all or some of them, into every known substance, were supposed to be not necessarily capable of individual existence themselves. This was the view held by the followers of Aristotle. With the reaction against the domination of the scholiasts, other views began to be held. It was Boyle who first gave voice to these changed views, in his "Sceptical Chemist" (1661). He defined elements as "certain primitive bodies, which, not being made of any other bodies, or of one another, are the ingredients of which all those called perfectly mixed bodies are immediately compounded, and into which they are ultimately resolved." He, however, did not believe himself warranted, from the knowledge then possessed, in claiming the positive existence of such elements.

But little attention was paid to the subject by the subsequent chemists. The phlogistics were too much occupied with their theory of combustion, and none could see the bearing of this question and its importance to exact science.

Macquer, in his "Dictionary of Chemistry" (1777) words his definition as follows:—"Those bodies are called elements which are so simple that they cannot by any known means be decomposed or even altered, and which also enter as principles or constituent parts into the combination of other bodies." To this he adds:—"The bodies in which this simplicity has been observed are fire, air, and the purest earth." In all of this may be observed the resolution of observed forms of matter into primal principles, following the dream of Lucretius and the early Epicurean philosophers, a dream abandoned by the atomic school following, though largely holding to the same definition.

It was only when chemists began to realise that mere observation of properties, chiefly physical, was not sufficient, that the subject began to clear up and lose its vagueness. Black proved that certain substances were possessed of a constant and definite composition and fixed properties, unalterable, and hence simple bodies or elements. Lavoisier finally cleared the way for the work of the nineteenth century by his definition that "an element is a substance from which no simpler body has yet been

* Address of the Vice-President before Section C—Chemistry—of the American Association for the Advancement of Science, at the Columbus Meeting, August, 1899.

obtained; a body in which no change causes a diminution of weight. Every substance is to be regarded as an element until it is proved to be otherwise." With this clear definition to build upon, a rational system of chemistry became, for the first time, a possibility.

Thus the elements were recognised as simple bodies because there were no simpler. They were not complex or compound. The distinction was clearly drawn between bodies simple and bodies compound, and the name simple body has been frequently used as a synonym for element through a large part of this century. Naturally the question of simplicity was first settled by an appeal to that great arbiter of chemical questions, the balance. And, quite as naturally, many blunders were made, and the list of bodies erroneously supposed to be simple was very large. All whose weight could not be reduced were considered elementary. When, however, from such a body, something of lesser weight could be produced, its supposed simplicity was, of course, disproved.

This test for the elemental character has been clung to persistently, and is perhaps still taught, although it was long ago recognised that many of the elements existed in different forms, a phenomenon to which Berzelius gave the name *allotropism*. One only of these could be simplest, and the others could be reduced to this one and rendered specifically lighter. With the discovery of this relation it should have been quite apparent that the old definition would no longer hold good. But many years passed before chemists were made to feel that a new definition was necessary, and adapted one to the newer knowledge.

The insight into what Lucretius would call "the nature of things" was becoming clearer; the mental grasp upon these elusive atoms about which the old Epicurean reasoned so shrewdly was becoming firmer. Through what one must regard as the veil interposed by the earlier idea of the element, the chemist began to grope after the constituent particle or atom. It must be borne in mind that the definition of the element was largely formulated before the resuscitation of the atomic theory by Dalton, and the mental picture of the one has perhaps retarded the clearing up of the ideas concerning the other. From the atomic point of view the element was next defined as one in which the molecules or divisible parts were made up of similar indivisible particles. This afforded an easy explanation of allotropism as a change in the number of atoms in a molecule. As Remsen says: "An element is a substance made up of atoms of the same kind; a compound is a substance made up of elements of unlike kind."

Laying aside, then, all vaguely formulated ideas of essences, or principles, or simple bodies, or elemental forms, we found our present building upon the conception of the ultimate particle, be this molecule or atom.

As to this atom some clear conception is needed, and here we come to the *crux* of the modern theories. The chemist regards this atom as a particle of matter, and is unwilling to accept the theory of Boscovich that it is infinitely small, and hence a mathematical point, nor can he admit that it is merely a resisting point, and hence that all matter is but a system of forces. And yet it seems as though some authorities would lead up to such a conclusion.

While we need not consider these atoms as mere centres of forces, we are compelled to study them by the operation of forces upon them. What are called their properties have been studied and recorded with great care. These properties are evinced in the action of the forces upon matter, and the exhibition of force without matter cannot be admitted. This study of the properties has been the especial occupation of the century now closing, and so the elemental atom has come to be regarded as a collection of properties. As Pattison-Muir puts it ("Alchemical Essence and the Chemical Elements," p. 31):—"The name copper is used to distinguish a certain group of properties, that we always find associated

together, from other groups of associated properties, and if we do not find the group of properties connoted by the term copper we do not find copper."

These properties are exhibited by the action of a small group of forces. Perhaps we do not know all of the forces; certain it is that we do not accurately know all of the properties, but, to quote Pattison-Muir again:—"The discovery of new properties always associated with a group of properties we call copper would not invalidate the statement that copper is always copper."

The properties of an atom are either primary, inherent and as unchanging as the atom itself, or they are secondary and dependent upon the influence of the other atoms, or varying with the change of conditions. To the first class belong such properties as the atomic weight, atomic heat, specific gravity, &c.; to the second, chemical affinity, valence, &c. In all the study of the atom the distinction between these should be carefully maintained in order that there may be clear thinking.

(To be continued).

OBITUARY.

GENERAL A. DE COURCY SCOTT, R.E.

WE regret to record the death, on Monday last week, at his residence in South Kensington, of Major-General A. de Courcy Scott, R.E., the Official Water Examiner under the Metropolis Water Act, 1871. Deceased received this appointment early in 1887, on the death of Sir Francis Bolton, who had filled the position of Water Examiner from the date of the passing of the Act. When the vacancy occurred, it was thought that the post would be offered to Dr. (afterwards Sir Edward) Frankland, but in giving it to an ex-officer of Engineers the Local Government Board probably wished to ensure a continuity of the practice instituted by his predecessor. General Scott was conversant with the London Water Question, having published a pamphlet entitled "London Water: A Review of the Present Condition and Suggested Improvements of the Metropolitan Water Supply;" and, further, he was an examiner in the Science and Art Department at South Kensington. He was one of the members of the present Royal Commission; and it is a singular circumstance that he is the second of that body who has been removed by death before the result of their investigations is made known—Mr. H. W. Cripps having died a short time ago. Moreover, the Local Government Board have lost, by the death of Sir Edward Frankland and General Scott, the two officials on whom they relied for advice on water questions. It only remains to say that deceased entered the Royal Engineers in 1853 as a second lieutenant, and was present at the siege of Sebastopol; receiving the medal with clasp and also the Turkish medal. He retired in 1884 with the rank of Major-General.—*Journal of Gas Lighting*.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 15, October 9, 1899.

Stereochemistry of Nitrogen.—J. A. Le Bel.—There seems to be no doubt that both optic and chemical isomerism exists in those derivatives of ammonium chloride, which include round the nitrogen atom four different radicles, and which contain six atoms of carbon at the least. Though the author's experiments, besides those of

Wedekind, have established the fact that bodies containing, at the least, six atoms of carbon have a stable geometric form, experiment has not yet been able to show whether this form is a pyramid with a square base or a double tetrahedron. The first hypothesis allows of three chemical isomers, the second of four, but at present only two are known; therefore all discussion on this subject is necessarily premature.

Reversible Liquefaction of Albumenoids.—M. Tsvett.—The author finds that various organic substances, such as the dioxybenzols (resorcine, pyrocatechin), phenol, chloral hydrate, &c., are susceptible of increasing the swelling up and the solution in water of many of the principal albumenoids. Under certain conditions of concentration the albumenoid matter passes, after swelling up, into the state of a true liquid. This solution in, and liquefaction of, albumenoids in aqueous resorcine is not connected with a chemical modification; the albumenoid will return to its original state by means of dialysis or precipitation by water. The phenomenon is, in fact, reversible.

Volumetric Estimation of Quinones derived from Benzene.—Amand Valeur.—The method of estimation which the author proposes is based on the reduction of the quinones by hydriodic acid. Instead, however, of using the free acid, an equivalent mixture of hydrochloric acid and potassium iodide is used. The results show that the action of this mixture on the quinones is instantaneous, and takes place according to the equation $C_6H_4O_2 + 2HCl + 2KI = C_6H_6O_2 + 2KCl + I_2$. The iodine liberated remains dissolved in the undecomposed iodide of potassium. It can be titrated with great accuracy by means of sodium thiosulphate.

MEETINGS FOR THE WEEK.

THURSDAY, Nov. 2nd.—Chemical, 8. "The Theory of Saponification," by J. Lewkowitsch. "The Action of Dilute Nitric Acid on Oleic and Elaidic Acids," by F. G. Edmed. "Tetrazoline," by Siegfried Ruhemann and H. E. Stapleton. "On Ethylic Dibromobutanetetra-carboxylate and the Synthesis of Tetra-hydrofurfural- α - α' -dicarboxylic Acid," by Bevan Lean, D.Sc., B.A. "Camphoroxime,"—Part III. Behaviour of Camphoroxime towards Potassium Hypobromite," and "Optical Influence of an Unsaturated Linkage on certain Derivatives of Bornylamine," by M. O. Forster, Ph.D., D.Sc.

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THE CHEMICAL NEWS.

VOL. LXXX., No. 2084.

A NEW RADIO-ACTIVE MATERIAL.

By A. DEBIERNE.

M. AND MME. CURIE have shown that the radio-active property of pitchblende is not only due to the uranium contained in the mineral. Examination of the different substances which this mineral contains have led to the conclusion that there are present two new radiant elements, polonium and radium, both more active than uranium.

Polonium is an element closely akin to bismuth, accompanying the latter in all chemical reactions, but from which it can be slowly separated by repeated fractionations.

Radium resembles barium in its chemical reactions, and again it is only by repeated fractionations that a separation can be effected.

The individuality of these new elements, revealed only by their radio-activity, has been confirmed in one case by M. Demarçay. It appears therefore that this property of emitting radiation is sufficient to characterise chemical elements. I have examined other radiant parts of pitchblende. My researches have been chiefly carried out on that portion of the acid solution of pitchblende which is not precipitated by sulphuretted hydrogen, and is precipitated completely by ammonia or ammonium sulphide.

The material with which I started was almost free from uranium. The quantity of radiant products contained in it appeared to be very slight; so the first part of the research consisted in working up a great quantity of the substance, many hundreds of kilogrms., and eliminating as completely as possible the known radiant matter (polonium and radium).

The major portion of the product precipitated by ammonia is composed of iron and aluminium oxide, but besides these substances I recognised the presence of a considerable number of others which are present in very small quantities. I then separated the little quantity of zinc, manganese, chromium, vanadium, uranium, titanium, niobium, and tantalum. There were present also some of the rare earths of which I recognised lanthanum, didymium, cerium, and the yttria earths.

The radio-activity, which exists in a slight degree in the total mass of the group precipitated by ammonia, is concentrated in certain parts in proportion as the separation is effected.

I then ascertained that the portion containing titanium and analogous bodies showed radio-activity in the most marked degree, and after a very complicated process, on the nature of which I shall speak later, I obtained a substance a solution of which showed the principal analytical properties of titanium, but which emitted extremely active rays.

The radio-activity of a fraction of this substance has been roughly determined as being five thousand times greater than that of uranium. Further, this substance has chemical properties entirely different from those of radium and polonium.

The rays emitted by the new substance are quite comparable with those which have been observed by M. and Mme. Curie from polonium and radium.

These rays render gases capable of discharging electrified bodies, they excite phosphorescence in barium platino cyanide and affect photographic plates.

The new substance is distinguished from radium in that it is not spontaneously luminous, M. and Mme. Curie having shown that radium emits a perfectly distinct light when placed in a dark room.

I hope shortly to publish further researches on this radio-active material.—*Comptes Rendus*, No. 16, October 16th, 1899.

ON THE ELECTROLYSIS OF SOLUTIONS OF CHLORIDE OF ZINC, AND THE NATURE OF THE DEPOSITS OF SPONGY ZINC.

By F. FÖRSTER and O. GÜNTHER.

STARTING from the hypothesis that the electrolytic deposition of spongy zinc is due to the presence of oxide of zinc precipitated on the cathode, the authors have made a certain number of experiments which confirm this supposition.

A zinc cathode was suspended in a perfectly pure neutral solution of chloride of zinc, containing 54.6 grms. of metallic zinc per litre. This cathode was placed between two anodes of pure electrolytic zinc.

With a current density of 1.4 ampères per square decimetre, a compact polished deposit of zinc was obtained for the first six hours, but after twenty hours spongy zinc was deposited, and the solution became cloudy on account of the presence of basic chloride of zinc in suspension.

On filtering off this precipitate, and replacing the old cathode by a fresh one, a good deposit was again obtained, but for a few hours only, when the electrolyte again became cloudy, and at the same time the deposit of zinc became spongy.

According to Schnabel ("Handbuch der Metallhüttenkunde," ii., p. 114), the formation of spongy zinc may be avoided by adding chlorine or chloride of lime to the electrolyte. The authors have tried the method described by Mylius and Fromm, which consists in keeping the solution of sulphate of zinc constantly acid. For this purpose they used two small anodes of platinum, from the surface of which they caused chlorine to be continually given off by connecting them with the positive pole of a battery consisting of two accumulators, while the negative pole was connected to the large zinc plate, which thus served as cathode for both pairs of anodes.

In neutral solution the above arrangement did not prevent the formation of spongy zinc.

The atmospheric oxygen easily oxidised the zinc in the presence of chloride of zinc, and a certain proportion of the oxide formed became dissolved in the electrolyte, giving basic chloride of zinc.

The formation of spongy zinc does not take place except when the excess of oxide commences to make the solution cloudy. If this precipitation is prevented by means of a periodical addition of hydrochloric acid, excellent deposits of zinc can be obtained. The authors, therefore recommend the addition of free hydrochloric acid to the electrolyte, in such proportion that the solution will be from $\frac{1}{20}$ th to $\frac{1}{30}$ th normal. In no case should it be allowed to become $\frac{1}{20}$ th or $\frac{1}{30}$ th normal.

By using a slightly acid electrolyte, and adopting the arrangement described above for giving off chlorine in the body of the solution, still better deposits are obtained. When the solution contains 0.2 gm. of free chlorine per litre, the hydrogen liberated at the cathode does not adhere to the electrode sufficiently long to affect the surface of the deposit.

But even when there is no doubt about the acidity of the mass of the solution, there arrives a time when spongy zinc is again deposited. This is due to the fact that the layer of the electrolyte in contact with the cathode loses its free acid; this inconvenience can, however, be remedied by keeping up a sufficient circulation of the solution.

The authors conclude by discussing the nature of the spongy zinc, and the effects obtained on adding certain

oxidising or reducing agents to the electrolyte. The addition of 1 per cent. of a perfectly neutral solution of persulphate of ammonium to a neutral solution of chloride of zinc enables very good deposits to be obtained. On the other hand, on adding 0.025 per cent of peroxide of hydrogen to the electrolyte, spongy zinc begins to form at the end of only ten minutes.—*Zeits. fur Elektrochemie*, v., [1], p. 16.

THE VOLUMETRIC ESTIMATION OF CARBON IN STEEL.

In a former paper (CHEMICAL NEWS, vol. lxxx., p. 52) the fact that combined and graphitic carbon separated from steel or pig-iron reacts best with respective mixtures of bichromate and sulphuric acid of definite percentage of sulphuric acid is briefly referred to. In amplification thereof the following tests were made:—

Combined Carbon.—The carbon was separated from 3 grms. of steel containing 1.18 per cent, and, after careful washing, was digested with 30 c.c. of a mixture of varying percentages of sulphuric acid and 0.7 gm. of dry powdered potassium bichromate. The digestions in the water-bath, made in batches of four, were stirred in rapid succession during a certain number of minutes. The asbestos filter and carbonaceous residue were sucked as dry as possible, but not otherwise dried. The results were as follows:—

Per cent H ₂ SO ₄ .	Percentage of carbon oxidised.	
	Digested thirty minutes.	Digested fifteen minutes.
10	0.58	—
20	0.77	—
30	0.90	—
40	1.05	—
50	1.17	1.04
60	1.19	1.12
70	1.20	1.08
80	1.10	0.81
90	0.59	—
100	0.35	—

Graphitic Carbon.—There is some difficulty in sampling a graphitic pig-iron so as to obtain concordant analytical results. Three results of assays made by the ordinary process gave 3.29, 3.47, and 3.16 per cent of graphite. This sample was sieved, and that portion retained which would pass through a 30 but not through a 60 mesh sieve. Three assays of this gave 1.45, 1.46, and 1.45 per cent graphite. As much of this sample as yielded graphite equal in weight to the combined carbon operated on was decomposed with nitric acid, and the residue treated as before with mixtures of bichromate and sulphuric acid. To facilitate comparison with the former series, the amount of graphite is calculated on to 3 grms., so that a complete combustion would give 1.18 per cent. The results were:—

Per cent H ₂ SO ₄ .	Carbon oxidised by digesting thirty minutes.
10	0.04
20	0.09
30	0.12
40	0.17
50	0.31
60	0.47
70	0.62
80	0.78
90	1.07
100	1.00

These results show that in combusting a carbonaceous residue by means of chromic and sulphuric acids the strength of the latter acid is a very important point; between 50 per cent and 70 per cent being most suitable for combined carbon and about 90 per cent the most suitable

for graphite, although where higher temperatures are available the combustion of graphite may be speedily accomplished with the weaker acids.

Decomposition of Heated K₂Cr₂O₇ + H₂SO₄.—Mixtures of chromic and sulphuric acid are known to suffer decomposition at about 105° C. and beyond. Cross and Bevan point out that this reaction is more rapid in mixtures of bichromate and sulphuric acid than in mixtures of chromic anhydride and sulphuric acid, and they hazard the opinion that the portion of CrO₃ remaining undissolved is more liable to decomposition than that dissolved in the acid (*Journ. Chem. Soc.*, liii., 894). Mixtures of bichromate and sulphuric acid are decomposed slowly at 100° C., or even several degrees lower. The results with varying strengths of sulphuric acid are very irregular—first reaching a maximum, and then declining. As illustrating the limitations of the volumetric process, this is an important point. In the following experiments 0.7 gm. of powdered K₂Cr₂O₇ was digested with 30 c.c. H₂SO₄ of the stated strength. The figures show the percentage of the added bichromate estimated after heating at the indicated temperature for three hours.

Per cent H ₂ SO ₄ .	130° C.	120° C.	110° C.	100° C. for sixteen hours.
30	100.0	—	—	—
40	100.1	—	—	—
50	100.1	—	—	99.9
60	98.6	99.2	99.6	99.9
70	91.3	98.2	99.0	99.6
80	88.7	95.1	96.5	98.1
90	91.3	95.8	96.8	98.2
100	94.8	—	—	97.6

In order to magnify the discrepancies obtained by heating for three hours at 100° C., a similar series were heated for sixteen hours (last column), when the small differences which might well have been due to experimental error turn out to be indications of a very slow decomposition. The results show that the decomposition is most energetic when the strength of sulphuric acid is about 80 per cent, and that 50 per cent to 60 per cent H₂SO₄ is the strongest acid permissible during prolonged heating. The conditions are not exactly those of a volumetric assay: there the reduction by the carbon rapidly lessens the amount of chromic acid and substitutes the corresponding amount of chromic sulphate; both these differences may favour the stability of the mixture. Although the perfectly stable solution made with 50 per cent sulphuric acid can accomplish, at the higher temperatures, all that is required in the particular branch of analysis being dealt with; many other strengths, even with three hours' digestion, introduce quite negligible errors when calculated into the few tenths or even units percentage of carbon metalliferous materials contain. Experiments in which the K₂Cr₂O₇ was retained as much as possible in the solid state gave results not appreciably different from similar experiments in which the K₂Cr₂O₇ was dissolved as far as possible; so that, for mixtures of K₂Cr₂O₇ and H₂SO₄, the state of the former reagents has little or nothing to do with the decomposition. Two other points repeatedly observed are that, after digestion, the cooled solutions deposited no crystals when the strength of H₂SO₄ was 50 per cent or less, or 80 per cent or more, but always in samples made up with the same volumes of 60 and 70 per cent H₂SO₄. The solubility, therefore, does not vary regularly with the strength of the sulphuric acid. In samples made up with 90 and 100 per cent H₂SO₄ the watch-glass was always covered with a solution of CrO₃, even when the digestions were made so far below the boiling-point of the mixture as 100° C. is. The volume of sulphuric acid used has very little influence on the speed of oxidation so long as enough is present to allow free movement of the carbon and filter in the oxidising mixture. This point was determined by digesting carbon from the previously used steel with equal amounts of K₂Cr₂O₇ and 30 and 60 c.c. of heated sulphuric acid for fifteen minutes at 100° C. The results were:—

Strength H ₂ SO ₄ . Per cent.	30 c.c.	60 c.c.
50	1.08	1.06
60	1.13	1.10
70	1.08	1.06

The results quoted in the former paper, nearly all of which were obtained by using 50 per cent H₂SO₄ solutions, are proof that no great loss is occasioned by CO being evolved along with the CO₂. No fear therefore need be entertained that in the ordinary moist combustion process, in which the CO₂ is absorbed and weighed, low results will be obtained on this account. Assuming that there is a trifling evolution of CO along with the CO₂, the mixture made with the weaker acid is about as likely to oxidise it as is the mixture made with the stronger acid, although neither at 100° C. or below would be very effective. Passed over heated CuO, a measured volume of CO yielded 0.0845 grm. of CO₂; passed steadily through a mixture made up with strong H₂SO₄, only 0.0020 grm. CO₂ was formed; with 70 per cent H₂SO₄, only 0.0016 grm.; and with 30 per cent H₂SO₄, only 0.0004 grm. As the carbon evolved as CO can be only 1 or 2 per cent of the total, the advantage of one strength of acid over another is not worth mentioning.

It is a matter of common experience that nickel crucibles are liable to become coated with soot, even in contact with non-luminous flames. As highly chromiferous materials are frequently opened up and otherwise manipulated in nickel vessels, these sooty deposits are a source of danger. Owing to the low atomic weight of carbon, a seemingly insignificant amount of soot would be disastrous if digested in an acid solution of chromic acid representing only a few decigrams. of the material.

J. T.

THE REACTION BETWEEN POTASSIUM CYANIDE AND METADINITROBENZENE.*

By W. R. HODGKINSON and Lieut. HOPE, R.A.

IN the *Berichte* for 1884 is an abstract from *R. Trav. de Pharm.* (xxiii., 205, 235) of a communication by Lobry de Bruyn on the Action of KCN on *m*-Dinitrobenzene. The result of the action is stated to be an oxy-ethyl-nitrobenzonitrile (1.2.6). This reaction is also referred to in Beilstein's "Handbuch."

This reaction has been repeated with a slight modification.

In the abstract above noted it is stated that an alcoholic solution of the dinitrobenzene was treated with KCN dissolved in a little water. We have employed the purest KCN obtainable, and as nearly absolute alcohol as ordinarily possible.

On digesting for a little time (40 minutes to 1 hour) on a water-bath, we noticed the formation of the purple-red colouring-matter and its change into brown. On cooling, a considerable crystallisation took place. The solid was separated from the excess of alcohol, and was found to dissolve for the most part in hot water. A small amount of blackish amorphous substance remained insoluble.

On acidifying the water solution a brown precipitate was formed. It was washed with cold dilute sulphuric acid and water and then dissolved in hot alcohol, from which crystals were separated on cooling and also on evaporation.

On analysis (N₂ only) figures have been obtained pointing distinctly to a nitrocyanide or nitrile, C₆H₅NO₂CN. Considerably more than 80 per cent of the reaction has gone in this line.

The same body has been obtained with dry methyl

alcohol and also with normal propylic alcohol as the solvents for the dinitrobenzene.

With acetone and paraldehyde as solvents, beyond the formation of a small amount of colouring-matter very little action could have taken place, for over 90 per cent of the dinitrobenzene was recovered and the KCN seemed scarcely acted on.

With an appreciable amount of water present and ordinary very alkaline cyanide the reaction probably runs quite differently.

With moderately dry and pure materials we have failed to obtain any sign of an oxy-ethyl or oxy-methyl derivative.

The nitrocyanide (or nitrile) forms brown needles from alcohol, which decompose (puff off) when heated to about 200°.

It does not seem to hydrolyse with KHO or on simply boiling with HCl.

We commenced this with a view of employing the oxy-ethyl mononitrile for another investigation, but now wish to re-investigate this reaction.

Ordnance College, Woolwich.

THE ACTION OF METALLIC MAGNESIUM ON WATER.

By EDWARD G. BRYANT, B.A., B.Sc. (Lond.).

THE references to this matter in chemical literature are, as far as I have been able to discover, very meagre and somewhat contradictory. The subject is dismissed in half-a-dozen words in most of the standard text-books, and I have not been able to find any account of original experiments. Yet it seems a point of some importance, as showing the relationship of magnesium to zinc on the one hand, and the alkaline earths on the other.

Gmelin's "Handbook" (Watts's translation, 1844), Watts's "Dictionary of Chemistry" (1892), and Dammer's "Handbuch der Anorganische Chemie," state that water does not decompose magnesium except at high temperature. Dammer gives Liebig and Bunsen as authorities, but I have not succeeded in finding any mention of the matter in the works of these two chemists.

On the other hand, Würtz's "Dictionary" says that magnesium slowly decomposes pure water, "l'eau pure," and that both carbonic acid and oxygen in the water accelerate the action. As far as oxygen is concerned, Gmelin supports this statement.

A chance experiment had led me to believe that the substances had a slight action on one another at ordinary temperatures, and the discovery of the above conflicting views induced me to carry out a series of observations as thorough as the means at my disposal permitted.

I find that magnesium and water react upon one another slightly at all temperatures; that the action depends very largely upon the amount of surface offered by the magnesium; that there is but slight difference in the amounts of gas evolved at boiling-point or in the cold; and that in all cases action ceases long before the magnesium has disappeared.

The magnesium used was the commercial metal, as I was quite unable to procure any in the pure state. Several samples were analysed qualitatively and one quantitatively; all, except one from Messrs. Johnson and Matthey, contained iron, with traces of zinc, aluminium, and calcium. The quantitative estimation of one sample gave:—

Iron	1.77 per cent.
Calcium	0.3

Messrs. Clowes and Caven found the best commercial metal pure enough for their experiments on the decomposition of copper sulphate; Villiers and Borg, also (CHEM. NEWS, lxviii., 263), speak of the high degree of

* Read before the British Association (Section B), Dover Meeting, 1899.

purity of ordinary magnesium. I further tested the metal for carbon, but without result; it dissolved perfectly in nitric acid, giving a colourless solution; also when dissolved in hydrochloric acid, and the gas evolved passed over pure copper oxide, no trace of carbon dioxide could be obtained. The results obtained from the various specimens when placed in water were indistinguishable whether iron were present or not.

The decomposition can be seen without the least difficulty by placing a few magnesium filings in a tube filled with water, and then inverting the tube in a small vessel of water. The powder is seen to become more and more flocculent, and after a few seconds the whole mass rises to the top. If it be shaken down a bubble of gas is left behind; masses of the filings keep rising and falling, and small bubbles ascend rapidly for some time. The action slackens after a few minutes, but abundant bubbles can be obtained by occasional shaking, even after an hour or two, and for many hours the action continues with continually less energy. The gas is pure hydrogen; on exploding with oxygen in excess, no trace of carbon dioxide could be found. The solution gives a strong alkaline reaction with phenolphthalein, and will usually give a cloudiness with ammonia and sodium phosphate. I could never find any calcium in solution. From 0.1 grm. of powder in 100 c.c. water, 2 to 3 c.c. of hydrogen can be obtained; from the same amount of metal, in 550 c.c. of water, 5.5 c.c. of hydrogen. On the basis of these figures the solubility of magnesium oxide in water can be roughly determined, and is found to be 1 part in 225,000 of water. If ribbon be used instead, the yield of gas is not more than one-fourth as much for the same amounts of metal and water. The colour of the metal is decidedly brownish-white after the experiment, and its lustre is greatly diminished. The water, if cold, never becomes clouded in the least degree, even after rapid shaking.

If the ribbon be cleaned with sand-paper (or the powder with 1 per cent HCl and thoroughly washed), the action re-commences on putting it back into the same water, much as at first, and this can be repeated as long as any metal remains; or, as a variation, an additional quantity of magnesium can be added to the water with like result.

Certain neutral salts, especially sodium sulphate, cause a much stronger action to take place, the yield of gas being three or four times as great. The solution also gives a much stronger precipitate of the ammoniac magnesium phosphate. Alcohol, on the other hand, has not the slightest effect on the metal until about 25 per cent of water has been added to it.

Magnesium powder placed in alcohol remains bright and inactive. If a quantity of water be added action starts, and can be renewed by the addition of more water. Lastly, if a few crystals of sodium sulphate be introduced, a much stronger action will commence almost immediately.

It is noteworthy that alcohol will not dissolve enough magnesium oxide to give a trace of colour with phenolphthalein; water dissolves enough to give a very faint precipitate with ammoniac phosphate and ammonia, while saturated sodium sulphate solution will give a very distinct precipitate.

Water dissolves such an inappreciable quantity of the oxide that the difference between the amounts of gas given with pure water and water saturated with the oxide, is, as might be expected, hardly measurable with ordinary apparatus. The difference in the case of sodium sulphate treated in the same way ought to be much larger, but I could not obtain the expected amount.

The action of magnesium on boiling water is more rapid, but is more quickly ended, the amount of gas evolved being very little larger than when cold water is used. The water and the containing vessel present a filmy white appearance when cold, as if a slight deposit of oxide had occurred.

The possible influence of gases and other impurities in the distilled water used was carefully examined. In the

first place, the quantity of gas evolved was proved to be almost exactly proportional to the amount of magnesium present, the volumes of water being equal. To make certain of the point, some water was re-distilled from alkaline permanganate, and before it had cooled was placed in a small flask and boiled. Some magnesium powder was placed in a second flask connected to the other by a glass tube. Carefully washed and dried coal-gas was passed over the magnesium and the boiling water. The magnesium was heated to 200° C. for half-an-hour, and the water kept boiling for the same time. The two end-tubes of the flasks were then instantly connected together, so that no oxygen could enter as the apparatus cooled. When cold, the water was poured over the magnesium. A brisk action started at once, and continued for the usual length of time. The experiment was repeated twice: (1) without heating the magnesium, (2) in pure hydrogen instead of coal-gas, as the latter might possibly have introduced some oxygen, but no difference could be detected in the action.

These experiments seem to prove conclusively that the oxygen or other gas in the water is not essential to the action. Since magnesium containing no carbon and no iron can decompose water, copper, silver, and other electro-negative metals being also absent, an electrical couple is also out of the question. Finally, no calcium could ever be detected in the solution, and the amount present in the magnesium is not sufficient to cause the evolution of more than a fraction of the hydrogen found. Magnesium has itself, I submit, the power to decompose water at all temperatures above 0° C., and the action is stopped by an insoluble coating of oxide forming on the metal. This would explain the change of colour seen after the action has ceased, the renewal of action when the surface is cleaned, and the more abundant evolution of gas from a solution of sodium sulphate, since magnesium oxide is more soluble in that than in pure water. I have not yet attempted to prove the presence or absence of a film of hydrogen on the metal in addition to the oxide. A film of this kind is well known in the case of zinc and sulphuric acid, and has been stated to form on aluminium (A. Ditte, *Comptes Rendus*, Dec. 5, 1898).

In conclusion, I wish to acknowledge my indebtedness to Prof. Smithells, for much help towards carrying out the experiments.

King's School, Pontefract.

LIQUID AIR AS AN ANALYTIC AGENT.*

By Professor DEWAR, M.A., LL.D., F.R.S.

(Concluded from p. 202).

Photographic Action at the Temperature of Liquid Air.

In a former lecture on "Phosphorescence and Photographic Action," it was shown that photographic action was reduced by 80 per cent at the temperature of -182° C. It was further proved that a sensitive film was still com-

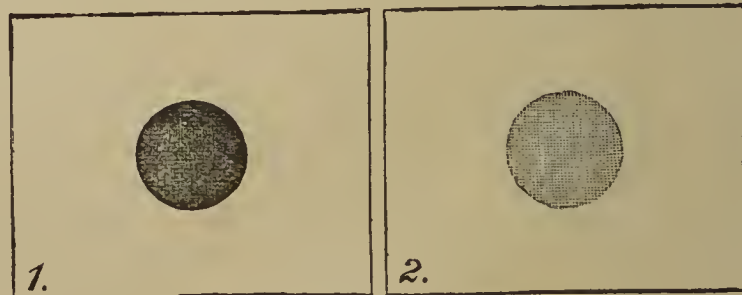


FIG. 5.

1, Photographic film exposed at ordinary temperature. 2, Photographic film cooled in liquid air during exposure. Both were exposed for the same length of time, and both were developed together.

* A Lecture delivered before the Royal Institution of Great Britain, April 1, 1898.

paratively active at the temperature of -210°C . Experiments in this direction have been continued at different times.

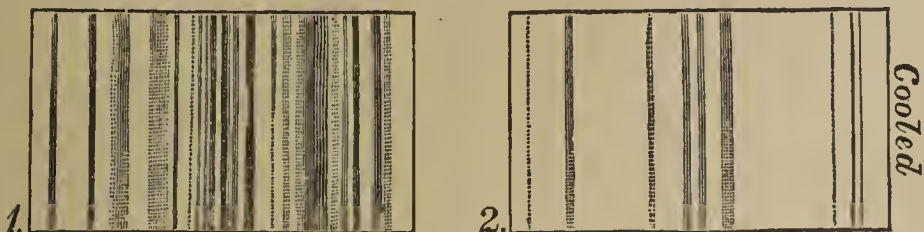


FIG. 6.—Ultra-violet Spectrum of Spark Discharge.

1, On film at ordinary temperature. 2, On film cooled in liquid air. Both exposed for the same length of time, and then developed together.

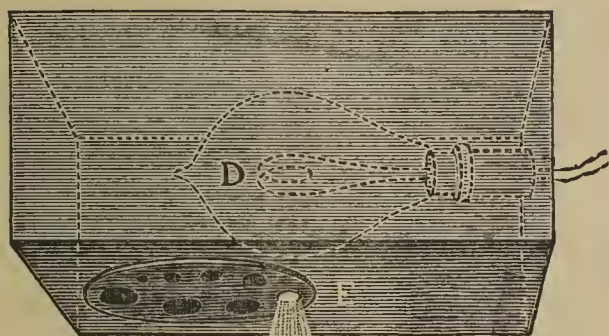


FIG. 7.

A, Vacuum cup with liquid air, into which is placed a photographic film in a small metallic slide having a hole in the centre. C, A metallic slide, holding a photographic film, which is exposed at ordinary temperature. Both of these are exposed to the light from a 16 candle-power lamp, D, contained in a box. The light is diminished or increased by the diaphragm at E.

In these new experiments the source of light was respectively a 16 candle-power lamp, a magnesium and cadmium spark discharge, and a Röntgen bulb. Small dark slides were prepared having a circular hole. One was placed in liquid air, and another simultaneously exposed for the same time at the ordinary temperature (FIG. 7). They were developed together, and the density of the image observed (Fig. 5).

Distance of Plates from Source of Light giving the same Photographic Intensity.

Source of light.	Cooled plate. In.	Uncooled plate. In.	Ratio of intensities at balance.
16 candle-power lamp	20	50	1 to 6
Ultra-violet spark magnesium and cadmium	22½	90	1 to 16
Röntgen bulb	10	24½	1 to 6

Further trials were made by bringing the cooled plate nearer to the source of light until finally a position was found where the very feeble photographic impression that appeared on both plates had the same density. In this position the relative distances of the plates from the source of light were measured. This mode of conducting the photographic comparison of the hot and cold plates gets over the difficulty of variation in the intensity of the source of light. From these experiments it would appear that when cooled to the temperature of liquid air both the incandescent lamp and the Röntgen radiation were reduced to 17 per cent of their photographic action at the ordinary temperature; whereas the ultra-violet radiation was reduced to about 6 per cent. This marked increase in the inertia of the photographic plate at low temperatures for the short-wave lengths cannot be explained by the absorption of liquid air, for such radiation as this is small for a thickness of 10 to 20 m.m. of the liquid. It is possible that the ultra-violet radiation is dissipated by the photographic film at low temperatures to a greater extent than with ordinary light, through absorption and subsequent emission as a phosphorescent glow. It would seem probable that if the plate could be developed at these low temperatures no action would be apparent, and that it is during the heating up after the low temperature exposure that the photographic action on the film takes place through an internal phosphorescence. This possibility must make us cautious in drawing inferences as to possible chemical action at low temperatures.

A more elaborate study of photographic and phosphorescent effects at low temperatures would add much to our knowledge of the chemical and physical actions of light.

THE DEFINITION OF THE ELEMENT.*

By F. P. VENABLE.

(Concluded from p. 207).

THERE is no field of mental activity requiring more faith than that of the chemist. He is dealing with the "evidences of things unseen." He must not be content with the mere gathering of facts, but divine what he can of their deeper meaning. Few chemists have had such insight as Graham into the significance of even the simplest changes. He was not content with mere surface observation. Even the commonest observed phenomena were to him full of meaning as to the atoms and their "eternal motion." Thorpe ("Essays in Historical Chemistry," p. 219) has drawn afresh the attention of the chemist to the thoughtful words of this great thinker. His mind was filled with the fascinating dream of the

* Address of the Vice-President before Section C—Chemistry—of the American Association for the Advancement of Science, at the Columbus Meeting, August, 1899.

unity of matter. "In all his work," says Adam Smith, "we find him steadily thinking on the ultimate composition of bodies. He searches after it in following the molecules of gases when diffusing; these he watches as they flow into a vacuum or into other gases, and observes carefully as they pass through tubes, noting the effect of weight, of composition, upon them in transpiration. He follows them as they enter into liquids and pass out, and as they are absorbed or dissolved by colloid bodies; he attentively inquires if they are absorbed by metals in a similar manner, and finds remotest analogies which, by their boldness, compel one to stop reading and to think if they really be possible.

In his paper entitled "Speculative Ideas respecting the Constitution of Matter," published in the *Proceedings of the Royal Society* in 1863, which Thorpe calls his "Confession of Faith," he tells of his conception that these supposed elements of ours may possess one and the same ultimate or atomic molecule existing in different conditions of movement.

It is not possible for me, in the limits of this Address, to array before you all of the various evidence which leads to the belief that our so-called elementary atoms are after all but compounds of an intimate peculiar nature whose dissociation we have as yet been unable to accomplish. When properly marshalled, it gives a very staggering blow to the old faith. Thorpe speaks of the "old metaphysical quibble concerning the divisibility or indivisibility of the atom." To Graham "the atom meant something which is not divided, not something which cannot be divided." The original indivisible atom may be something far down in the make-up of the molecule.

How shall the question as to the composite nature of the elements be approached? The problem has been attacked from the experimental side several times during the last half century, but the work seems to have been carried on after a desultory fashion and was soon dropped, as if the workers were convinced of its uselessness. The results, being negative, simply serve to show that no method was hit upon for decomposing the elements upon which the experiments were performed. Thus, for instance, Despretz performed a number of experiments to combat Dumas' views as to the composite nature of the elements. Despretz made use of the well-known laboratory methods for the separation and purification of substances. Such were distillation, electrolysis, fractional precipitation, &c. Such work was quite inadequate to settle the question, as Dumas had pointed out that unusual methods must be used, or, he might have added, the old methods carried out to an unusual or exhaustive extent. Certainly, if a moderate application of the usual methods was sufficient for this decomposition, evidences of it would have been obtained long ago by the host of careful workers who have occupied themselves over these substances. Crookes has busied himself with the method of fractional precipitation (though not with special view to the testing of this question), and applied it most patiently and exhaustively to such substances as the rare earths, without obtaining results from which anything conclusive could be drawn. Victor Meyer seems to have believed that the decomposition could be effected by high temperatures, and was very hopeful of experiments which he had planned before his untimely death. Others have spasmodically given a little time to the problem, but no one has thought highly enough of it to attack it with all of his energy.

Let us stop a moment and ask ourselves what would be attained if any one should succeed in decomposing an element by one of the usual methods. Has not this been done repeatedly in the past and merely served to add to the list of the elements? Didymium has been made to yield praseo and neodmium. That which was first called yttrium has been divided into erbium, terbium, and ytterbium, and according to Crookes may possibly be still further decomposed. But these and similar decompositions are not generally accepted as offering any evidence

that elements can be decomposed. It is merely the discovery of one or more new substances which have remained hidden in constant association with known bodies which were supposed to be simple. It would be necessary to prove that a single individual element had, by the process adopted, been actually decomposed and not some pre-existing impurity discovered. This, of course, would be exceedingly difficult, and all such attempts as those mentioned can have little bearing upon the general question, and can hold out slight hope of reward beyond the fame springing from the discovery of a new element.

Successful decomposition should mean much more. It should mean the discovery of a method which will decompose not one, but many, or indeed all of the elements, and the decomposition of these must not yield a larger number of supposedly simple bodies, but a small group of one or two or three which are common constituents of all. It is quite idle to venture upon any prediction whether such a method will ever be discovered. Setting aside, then, the direct experimental proof of the composite nature of the elements as unattainable at present, let us next examine the indirect evidence. It would seem wisest for the present to introduce under that heading the spectroscopic work of Lockyer. The results, while highly interesting, are too indefinite as yet to speak of as having a direct bearing. Yet a careful study of the spectra of the elements leads us to a strong suspicion that the less plausible assumption is the one that the particles which give rise to such varied vibrations are simple and unitary in nature. Lockyer's most recent work, following up the line of his "Working Hypothesis" of twenty years ago, is very suggestive, and may lead to important results ("Chemistry of the Hottest Stars," *Roy. Soc. Proc.*, lxi., 148; "On the Order of Appearance of Chemical Substances at Different Temperatures," *CHEM. NEWS*, lxxix., 145). Still too much must be assumed yet for such work to be very conclusive. He writes of "proto-magnesium and proto-calcium," and Pickering discusses a "new hydrogen," all with an assurance and confidence which proves at least how deeply these changes in the spectra have impressed some of those who have most deeply studied them.

But a more important method of indirectly testing the question is through a comparison of the properties of the atoms. Such a comparison has been made as to the atomic weights. In other words, the idea of the composite nature of the elements followed very closely upon the adoption of a stricter definition of them as simple bodies. Dalton, Prout, Döbereiner, Dumas, Cooke, and many others, have aided in developing the idea, sometimes faultily and harmfully, at other times helpfully. Some fell into the common error of going too far, but all were struck by the fact that when these combining numbers, or atomic weights, were compared, strange and interesting symmetries appeared. The times were not ripe for an explanation of their meaning, and such crude assumptions as that of Prout, that the elements were composed of hydrogen, or that of Low, that they were made up of carbon and hydrogen, were too baseless to command much genuine support or to withstand much careful analysis. The important feature of agreement between such theories was the belief that the elements were composite and had one or more common constituents.

From the comparison of one property, the atomic weights, the next step was to the comparison of all the properties. This comparison is brought out clearest and best for us in the Periodic System. Here all the properties are very carefully tabulated for us. The study of the system leads indisputably to the conviction that this is not an arbitrary, but a natural arrangement, exceedingly simple in its groundwork, but embodying most fascinating symmetries, which hint of great underlying laws. He who looks upon it as a mere table of atomic weights has lost its meaning. It tells, with no uncertain note, of the kinship of the elements, and leads to a search after the secret of this interdependence and of their common factor

or factors. There is so much which is made clearer if we assume a composite nature for the elements that many do not hesitate to make the assumption.

Still another indirect method of approaching that problem is by analogy with bodies whose nature and composition are known. A very striking symmetry is observed between the hydrocarbons, and these in the form of compound radicals show a strong resemblance to certain of the elements. This analogy need not be dwelt upon here. It has been recognised for a long time, and tables of hydrocarbons have been constructed after the manner of the Periodic System. Now these bodies are simply built up of carbon and hydrogen in varying proportions, and in any one homologous series the increments are regular. We know that they are composite, and that they have but two common factors, carbon and hydrogen.

Again, the fact that certain groups of associated atoms behave as one element and closely resemble known elements may be taken as a clue to the nature of the elements. Thus carbon and nitrogen, in the form of cyanogen, behave very much like the halogens; and nitrogen and hydrogen in the form of ammonia so closely resemble the group of elements known as the alkalis that this "volatile alkali" was classed with them before the era of our elements and the analogy led to a vain search for an "alkalising principle," and later to an equally futile pursuit of the metal ammonium.

A further clue to this nature is afforded in the remarkable changes of properties which can be brought about in some elements by ordinary means, and one might mention the equally remarkable veiling of properties induced by the combining of two or more atoms. Thus copper exists in a cuprous and a cupric condition, and the change from one to the other can be readily brought about. And this is true of many other elements.

This has doubtless been a tedious enumeration to you of well-known facts and arguments, but it has been necessary, for I wish to lead you to the summing-up of these arguments and to induce you to draw boldly the necessary deductions. It is high time for chemists to formulate their opinions in this matter. It would seem as if we were shut up to one or two conclusions. Either these imagined simple bodies are after all compounds, built up of two or more common constituents, or they are but varying forms of one and the same kind of matter subjected to different influences and conditions. The supposition that they are distinct and unrelated simple bodies is, of course, a third alternative, but to my mind this is no longer tenable.

The second hypothesis is the one put forth by Graham. It was his cherished vision of the gaseous particles about which he thought so deeply, and in many ways so truly. Thorpe has written of this as follows (*loc. cit.*, 222):—

"He conceives that the various kinds of matter, now recognised as different elementary substances, may possess one and the same ultimate or atomic molecule existing in different conditions of movement. Graham traces the harmony of this hypothesis of the essential unity of matter with the equal action of gravity upon all bodies. He recognises that the numerous and varying properties of the solid and liquid, no less than the few grand and simple features of the gas, may all be dependent upon atomic and molecular mobility. Let us imagine, he says, one kind of substance only to exist—ponderable matter; and, further, that matter is divisible into ultimate atoms, uniform in size and weight. We shall have one substance and a common atom. With the atom at rest the uniformity of matter would be perfect. But the atom possesses always more or less motion, due, it must be assumed, to a primordial impulse. This motion gives rise to volume. The more rapid the movement, the greater the space occupied by the atom, somewhat as the orbit of a planet widens with the degree of projectile velocity. Matter is thus made to differ only in being lighter or denser matter. The specific motion of an atom being inalienable, light matter is no longer convertible into

heavy matter. In short, matter of different density forms different substances—different inconvertible elements, as they have been considered."

The hypothesis that the elements are built up of two or more common constituents has a larger number of supporters and would seem more plausible. Some have supposed one such primal element by the condensation or polymerisation of which the others were formed. Thus we have the hydrogen theory of Prout, modified to the one-half atom by Dumas, and finally by Zängerle to the one-thousandth hydrogen atom. The suggestion of Crookes as to the genesis of the elements from the hypothetical protyle, under the influence of electricity, may also be mentioned here.

Others have adopted the supposition of two elements, Reynolds making one of these an element with a negative atomic weight, whatever that may mean. Low and others have fixed upon carbon and hydrogen as the two elements.

There are many practical difficulties in the way of these suppositions; the lack of uniformity in the differences between the atomic weights, the sudden change of electrochemical character, and the impossibility, so far, of discovering any law underlying the gradation in the properties of the elements with the increase of atomic weights, are some of the difficulties. In comparing these two hypotheses that of Graham seems to me very improbable. I have thought of valence as dependent upon the character of the motion of the atom, but cannot well conceive of a similar dependence of atomic weight and all the other properties. There remains, then, the hypothesis of primal elements by the combination of which our elements have been formed. These molecules are probably distinguished from the ordinary molecules by the actual contact and absolute union of the component atoms without the intervention of ether.

Since these elemental molecules cannot as yet be divided, we may retain the name atom for them, but the idea of simplicity and homogeneity no longer belongs to them. The definition of an element as a body made up of similar atoms is equally lacking in fidelity to latest thought and belief, but chemists would scarcely consent to change it, and, indeed, it may well be retained, provided the modified meaning is given to the word atom. But, after all, an element is best defined by means of its properties. It is by close study of these that we decide upon its elemental nature, and through them it is tested. Complete reliance can no longer be placed upon the balance and the supposed atomic weight.

All elements are acted upon by gravity and chemical force and other physical forces, but within the last few years certain gaseous elements have been discovered which are not influenced by chemical force or affinity. According to some (Piccini, *Zeits. An. Chem.*, xix., 295) this necessitates a division of the elements into two classes. Manifestly, since it is chiefly by the action of chemical force that we study the elements, the absence of such action cuts us off from our chief means of finding out anything about them, and it is equally clear that bodies so diverse cannot well be classified together. If all attempts at bringing out the chemical union of these gaseous elements with other bodies fail, I believe that we should insist upon the existence of two classes of elements, and keep them distinct in all comparisons.

Of course we are quite at a loss to say just what chemical force is, but it is believed to be determined by the electrical condition of the atom. Thus we have the elements which show the action of chemical affinity varying from strongly electro-positive to strongly negative. This electrical charge of the atom seems to be a primitive, inherent property, and so beyond our control or power to change. At least no change of the kind has ever been recognised and recorded. Sodium remains positive and chlorine negative, in spite of all that may be done to them. We can, by uniting the two temporarily, cloak and neutralise

their opposite natures, but the original condition returns on their release.

Is it not fair to assume that argon, helium, and their companion gases, having no affinity, are without electrical charge—atoms from which the electrical charge has been withdrawn; the deadest forms of inanimate matter? Were they thus without electro-chemical properties and affinity from the beginning, or did they start out as ordinary atoms (if I may so call them), and somehow, somewhere lose these properties, and with them the power of entering into union of any kind, even of forming molecules, doomed to unending single existence? Can these be changed atoms of some of our well-known elements, a step nearer to the primal elements and with the electrical charge lost? Is it possible for us to bring about these changes? May we not unwittingly have done so at some time or other in the past? Is it possible to restore the electrical charge to such atoms, and so to place them once more on a footing of equality with elements of the conventional type? These and many other questions surge through the mind as one thinks of these wonderful gases. Perhaps the coming century will unfold the answers.

PHOTO-CRYSTALLISATION.*

By FERDINAND G. WIECHMANN, Ph.D.

LIGHT is one of the forms taken by the radiant energy which emanates from the sun. It is well known that light—or possibly some other form of energy accompanying light—is able to bring about about chemical and physical changes.

The influence of sunlight on sugar solutions has been noted at various times and by different observers. The earliest reference to an instance of this kind seems to be contained in an article published by Dr. C. Scheibler in 1861-62 in the *Jahresbericht über die Untersuchungen und Fortschritte auf dem Gesamtgebiete der Zuckerfabrikation*, vols. i. and ii., p. 194.

Some years ago the present writer noticed an interesting case of photo-action. A solution of partially inverted sucrose was, under the influence of sunlight, transformed into a crystalline solid. This change in the state of aggregation was accompanied by chemical change; the original amount of invert sugar in the solution, 84.8 per cent, was increased to 97.06 per cent. A memorandum of this observation was published at the time (*School of Mines Quarterly*, vol. xiii., No. 2), and as the matter seemed to warrant further and more careful study, after some preliminary trials, a series of experiments was planned and commenced in December, 1891. The observations then begun have extended over a period of four years, and a record of the work done is herewith given. In this connection it is a pleasant duty to acknowledge the valuable services of Mr. Edward C. Brainerd, to whom the writer is indebted for the analytical data presented.

The term photo-crystallisation, under which this article appears, has been coined by the writer because this word seemed to indicate most accurately the nature and character of the phenomena studied.

Photo-crystallisation has been observed in solutions of sucrose, partially inverted, and in plates of solid (barley) sugar. This communication will, however, deal only with the investigation of the sucrose solutions. These sucrose solutions were made by dissolving 64 parts by weight of perfectly pure sucrose (polarisation 100) in 16 parts by weight of distilled water; this gave an 80 per cent solution.

Partial inversion of this sucrose was effected by chemically pure hydrochloric acid, of specific gravity 1.20. Of this, an amount was used equivalent to 0.025 per cent of

* *School of Mines Quarterly*, vol. xvii., No. 4.

TABLE I.

SERIES I.—Exposed to Direct Sunlight.

State of crystallisation after — days.	Specimen numbers.					
	1.	2.	3.	4.	5.	6.
	90.9. Acid.	90.9. Neutral.	80.6. Acid.	80.6. Neutral.	58.0. Acid.	58.0. Neutral.
100	A	D	B	C	E	F
						No crystals.
135	Solid.	B	A	B	B	C
						No crystals.
170	..	B	A	B	B	C
						No crystals.
225	..	B	Solid.	C	A	D
						No crystals.
324	..	Solid.	..	Solid.	A	B
						Two small crystals.
365	Solid.	A
						Seven small crystals.
531	A
						Crystals throughout li- quid. About 1/3 of bottom of flask covered thinly by crys- tals.
628	A
						Crystals a through solu- tion.
785	A
						Ditto.
1095	A
						Ditto.
1473	A
						Crystals al- through mass. A semi-solid magma.

the weight of the dry sucrose employed, and equivalent to 0.02 per cent of the weight of the solution.

The sucrose was dissolved at the lowest possible temperature, not above 90° C. The solution was cooled down to 80° C. and then the hydrochloric acid was added. Inversion was completed at 80° C., the different amounts of invert sugar produced in the different solutions being secured by maintaining these solutions at the temperature named for a longer or shorter period of time.

The solutions thus prepared contained inverted sucrose to the extent of—

Solution A = 90.9 per cent
 „ B = 80.6 „
 „ C = 58.0 „

Each of the three solutions was divided into halves, thus giving rise to—

Solutions A I., A II.
 „ B I., B II.
 „ C I., C II.

Solutions A I., B I., C I. were left as prepared, very slightly acid; Solutions A II., B II., C II. were carefully neutralised with sodium bicarbonate, methyl-orange being the indicator used.

These solutions were placed into eighteen white glass flasks, which were securely corked after introduction of the solutions. They were divided into three groups, each

TABLE II.

SERIES II.—Exposed to Diffuse Daylight.

Specimen numbers.

State of crystallisation after — days.	7. 90°9. Acid.	8. 90°9. Neutral.	9. 80°6. Acid.	10. 80°6. Neutral.	11. 58°0. Acid.	12. 58°0. Neutral.
100	A	E	B	D	C	F No crystals.
135	A	E	B	D	C	F No crystals.
170	A	E	B	D	C	F Two small crystals.
225	A	E	B	D	C	F Ditto.
324	A	E	D	C	B	F Ditto.
365	B	E	D	C	A	F Ditto.
531	B	D	C	A	A	E About thirty crystals on bottom of flask.
628	B	C	D	Solid.	A	E
785	A	A	B	..	Solid.	C Fine crys- tals all through the solution.
1095	Solid.	..	A	B Crystals all through solu- tion, and layer of crystals on bottom $\frac{1}{2}$ inch thick.
1473	A	B Crystals all through the mass; semi- solid.

group consisting of the following six specimens, which contained respectively:—

Inverted sucrose	90°9	per cent	Slightly acid.
"	"	90°9	Neutralised.
"	"	80°6	Slightly acid.
"	"	80°6	Neutralised.
"	"	58°0	Slightly acid.
"	"	58°0	Neutralised.

The three sets were numbered respectively from 1—6, 7—12, 13—18. Set 1—6 was exposed to direct sunlight, as far as the condition of the laboratory in which the work was done permitted; exposure of the laboratory was south-west. Set 7—12 was placed in diffuse daylight, but shielded from all direct sunlight. Set 13—18 was kept in a dark closet, from which, however, diffuse daylight was not absolutely excluded during all of the time, as the door had occasionally to be opened to remove articles from or place articles into the closet; still, practically, it was kept in darkness. These three sets were under continuous observation, and the accompanying tables show the manner in which crystallisation progressed in the solutions.

The letters A, B, C, D, E, F employed in the tables are intended to indicate only the *relative* extent to which crystallisation had advanced in any given set of specimens at the time when the observation was made. The letters of one series cannot be compared directly with those of another series, nor taken as expressing

TABLE III.

SERIES III.—Kept in Darkness.

Specimen numbers.

State of crystallisation after — days.	13. 90°9. Acid.	14. 90°9. Neutral.	15. 80°6. Acid.	16. 80°6. Neutral.	17. 58°0. Acid.	18. 58°0. Neutral.
100	E	C	A	B	D	F No crystals.
135	E	D	A	B	C	F No crystals.
170	E	D	A	B	C	F No crystals.
225	E	D	A	C	B	F No crystals.
324	E	C	A	D	B	F No crystals.
365	E	C	A	D	B	F One crystal.
531	D	B	A	C	B	E Six crystals on bottom.
628	E	B	A	D	C	F
785	D	A	B	C	C	E
1095	C	Solid.	A	B	B	D A few crys- tals on bot- tom, all the rest is liquid.
1473	D (a)	..	A (b)	C (c)	B (d)	E Ditto.

(a) Half solid; liquid colour of amber.

(b) Almost solid.

(c) Nine-tenths solid; liquid of pale amber colour.

(d) Very nearly solid. Sides hard, central portion a magma.

that the same degree of crystallisation had been attained in both series. Wherever, however, one and the same letter is used for more than one specimen in the same series, this signifies that crystallisation had advanced to an equal degree in the specimens thus marked.

Although the time of growth of the crystals in the various solutions differed greatly, the manner of growth was the same in all cases. The first crystals made their appearance in the body of the solution and settled to the bottom of the flask. Then the crystals began to grow upwards on the sides of the flask, the interior portion of the solution remaining fluid the longest.

The growths consisted of snow-white crystalline nodules, which, through aggregation, gave rise to fern-like forms.

(To be continued).

Synthesis of Alcohol.—M. Berthelot.—The author confirmed previous theoretical considerations when he proved experimentally the regeneration of alcohol by means of pure olefiant gas, and showed that the body obtained has the same physical and chemical properties of ordinary alcohol. This was confirmed still more definitely by the direct synthesis of compounds of olefiant gas with the hydracids—that is to say, hydrochloric, hydrobromic, and hydriodic ethers—and from this he has devised a general method for the synthesis of derived alcohols and all the carbides of the same series. Finally, the direct synthesis of acetylene from the elements carbon and hydrogen, then the synthesis of olefiant gas from acetylene, has enabled the author to effect experimentally the complete synthesis of alcohol from the elements.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 8.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, October 27th, 1899.

Prof. W. E. AYRTON, F.R.S., Vice-President, in the Chair.

DR. S. W. RICHARDSON read a paper "*On the Magnetic Properties of the Alloys of Iron and Aluminium.*"

Observations were made upon four alloys containing respectively 3.64, 5.44, 9.89, and 18.47 per cent of aluminium. The alloys were used in the form of anchor rings, and were wound with primary and secondary coils separated by asbestos paper. The temperatures used ranged from -83°C . to 900°C . The low temperatures were produced by the rapid evaporation of ether, surrounded either by ice and salt or by carbon dioxide snow. The high temperatures were obtained either electrically or by gas muffles. In both cases the actual temperatures were deduced from the resistance of the secondary, which was made of platinum wire and wound next the metal. The author employed Maxwell's null method of measuring mutual induction, increasing the sensitiveness by the introduction of a secohmmeter making about three revolutions per second. In order to test the accuracy of the method some of the experiments were repeated with a ballistic galvanometer in the ordinary way, and the agreement obtained between the results in the two cases was well within the limits of experimental error. The chief conclusions to be drawn from the experiments may be summed up as follows:—(1). The alloys behave magnetically, as though they consisted of two distinct media superposed. (2). The general roundness of the curves and their lack of abruptness near the critical point seems to indicate that the alloys are heterogeneous in structure. (3). The permeability decreases with rise of temperature near the critical point until a minimum value is reached, when further rise of temperature produces very slight diminution, if any, in the permeability. (4). The experiments suggest that the maximum value of the permeability for an alloy containing 10 per cent of aluminium is reached at about -90°C . (5). An alloy containing 18.47 per cent of aluminium has a critical point at about 25°C . and gives no indication of temperature hysteresis. This alloy probably has a maximum permeability much below -90°C . The author has found that at high temperatures there is a second maximum in the induction curve. This maximum becomes less and less noticeable as the field is increased.

The SECRETARY read a note from Prof. BARRETT "*On the Electric and Magnetic Properties of Aluminium and other Steels.*" The first part of the note dealt with the electrical conductivity of various alloys, and discussed the effect of composition and annealing upon the value of the conductivity. The second part of the note referred to magnetic effects. The most remarkable effect produced by aluminium on iron is the reduction of the hysteresis loss. The permeability of nickel steels is shown to be very much influenced by annealing. It is found that the addition of a small quantity of tungsten to iron hardly affects the maximum induction, yet increases the retentivity and coercive force. The experiments show that the best steel for making permanent magnets is one containing $7\frac{1}{2}$ per cent of tungsten. The magnetometric method was employed throughout.

Prof. S. P. THOMPSON drew attention to the wide range of temperature over which the author had conducted his experiments, and also to the small number of alloys used. He said a very much finer connection between the properties could be obtained from the examination of more alloys, and expressed his interest in the existence of the second maximum on the induction curve. He would like to know how the percentage composition of the alloys had

been determined. Turning to Prof. Barrett's note, Prof. Thompson referred to the difference in the breadths of the hysteresis curves for aluminium and chromium alloys.

Mr. APPEYARD asked for information upon the permanence of the curves.

Dr. RICHARDSON, in replying, said the compositions were determined by analyses made after the experiments had been performed. It was proposed to carry on the research upon a series of aluminium alloys which he had obtained.

The CHAIRMAN expressed his special interest in the agreement which the author had obtained between the ballistic method and the null method of Maxwell, increased in sensitiveness by the secohmmeter.

Mr. ADDENBROOKE exhibited a Model illustrating a number of the Actions in the Flow of an Electric Current. The model consisted of a spiral of steel wire in the form of a closed circuit. Inside the spiral was placed a wire which was supposed to be carrying the current, and which directed the motion of the spiral. A rotational movement given to one part of the spiral was transmitted by the wire and produced a rotational movement at another part of the spiral. The resiliency of the spring represents capacity, and the torque electromotive force. Self-induction can be represented by weighing the spring.

Prof. EVERETT expressed his interest in the way that the correspondence between the propagation and the rotation agreed with that between the direction of a current and the direction of the magnetic force.

Prof. S. P. THOMPSON agreed that many analogies could be worked out by the model, but gave one or two examples to show that erroneous conclusions might be drawn by pushing the analogy too far.

Mr. W. WATSON repeated some Experiments with the Wehnelt Interrupter devised by Prof. Lecher. The experiments showed, in a clear and striking manner, the fact that subsequent sparks tend to pass through the portion of air heated by the first one. In the first experiments motion of the heated air was caused by differences in density, and in the later experiments by allowing the sparks to take place in a strong electro-magnetic field. The continuous rotation of the spark in a given field proved the unidirectional nature of the discharge. In reply to Mr. Blakesley, Mr. Watson said he used the word "ionised" in his explanations to express simply the fact that the air had been rendered a conductor by the passage of the spark.

The CHAIRMAN referred to one of the first experiments performed. In this experiment the electrodes consisted of two copper wires in a vertical plane, slightly inclined to one another, and nearest together at their lowest points. On switching on the current the spark passed between the lowest points, but as the ionised air ascended so did the most conducting path, and consequently the spark worked its way to the top of the electrodes. Here the heated air passed away, and the spark returned to the lowest point to rise again. The Chairman thought that these effects might be due to the magnetic force produced by the circuit itself. That similar effects in the arc light were due to this cause had been proved many years ago.

Mr. WATSON repeated some of the experiments under new conditions, and proved that the explanation of the phenomena was not to be found in the tendency of the circuit to enlarge itself owing to magnetic forces.

Mr. BOYS pointed out that the relation of the heating effect to the current, which was small in the arc light, was very large in the case of the spark discharges used, and therefore the movement of the spark in the latter case was practically determined by the heating effect in consequence of the relatively small importance of the electro-magnetic effect.

Prof. S. P. THOMPSON remarked that similar effects could be produced by an alternating current working an ordinary induction-coil.

The Society then adjourned until November 10th, when the meeting will be held in the Central Technical Institute.

NOTICES OF BOOKS.

Index to the Literature of Thallium, 1861—1896. By MARTHA DOAN. Smithsonian Miscellaneous Collections, No. 1171. Washington City, 1899. Pp. 26. 8vo.

THIS contribution to chemical bibliography bears the endorsement of the Committee on Indexing Chemical Literature appointed in 1882 by the American Association for the Advancement of Science. It presents in chronological order the most important references to papers on thallium and its compounds found in a large number of periodicals. This compilation is the first of the series that bears the name of a woman. Miss Doan was a student at Cornell University, in New York State.

An author-index completes the work.

School Chemistry. By CHARLES BASKERVILLE, the University of North Carolina. Richmond, Va.: B. F. Johnson Publishing Co. 1899. Pp. 159. 12mo.

THIS elementary work is the outcome of five years' experience in teaching teachers in the summer school of the University of North Carolina. The course is planned to cover forty weeks when one hour per week is devoted to it; of this hour, only thirty minutes is given to the performance of experiments, fifteen being given to reading aloud by the pupils the daily lesson, and fifteen to questioning them on the preceding lesson. The book is notable for the very large number of topics briefly treated.

A few slips may be corrected in a second edition: the "lunar caustic" used as a cautery is not crystalline, but fused silver nitrate. The simple experiments seem to be well chosen, and all the apparatus needed for ten pupils to carry them out can be bought in New York for 25 dollars.

Descriptive Chemistry. A Text-book for Short Course. By S. E. TILLMAN. Second Edition. New York: John Wiley and Sons. London: Chapman and Hall, Lim. 1899. Pp. x.—429. 8vo. Ill.

COLONEL SAMUEL E. TILLMAN, U.S. Army, has been for many years giving instruction in chemistry, mineralogy, and geology to the cadets at the U.S. Military Academy, West Point, N.Y. The time allowed for chemistry by the Faculty is only two months, or about two hundred hours for instruction, study, and other work on the subject, and the Professor is of the opinion that, under these limitations, "the unique disciplinary training for which chemistry is so admirably adapted as a laboratory science can only be very imperfectly attained." And therefore he is obliged to make the acquisition of knowledge the essential feature in the curriculum; this is secured by careful study of the proper text, well-conducted recitations, and explanatory lectures illustrated with experiments. Hence this text-book, which "aims to give a concise statement of the more fundamental principles of chemistry, together with that class of chemical information most essential to cultured men." The first chapter contains the principles of chemistry in language not too difficult to be grasped by fairly equipped students. The second chapter discusses the causes influencing chemical processes, and a statement of the Periodic Law; then follow chapters on the non-metals and metals. About one-fourth of the book is taken up with organic chemistry and the applications of chemistry. Under the latter heading there are sections on glass-making, pottery, explosives, coal-gas, beer, wine,

distilled liquors, bread, soap, leather, cheese, and dyeing. Throughout the handsomely printed volume two sizes of type are used; the smaller for less important matter. The illustrations are from original drawings made by Colonel Tillman's assistants.

The West Point Professor has produced an admirable book, written in clear, forceful style. The arrangement is one that appeals to common sense, and the selection of material is made with judgment. The author is conservative, and introduces no impracticable novelties. The book ought to find a wider field than the embryo army officers, especially as it has little distinctively military. To one word the reviewer takes exception—"stochiometry" as a substitute for the correct form stoichiometry (*stoicheion*).

Teachers having no fads will welcome this excellent book.

Indicators and Test-papers: their Source, Preparation, Application, and Tests for Sensitiveness. A *résumé* of the current Facts regarding the Action and Application of the Indicators and Test-papers which have been proposed from time to time and are in Present Use in Chemical Manipulations. With a Tabular Summary of the Application of Indicators, designed for the Use of Chemists, Pharmacists, and Students. By ALFRED I. COHN. New York: John Wiley and Sons. London: Chapman and Hall, Lim. 1899. Pp. x.—249. 12mo.

THIS volume has so many words on the title-page that it leaves little for the reviewer to do besides making the statement that the author has carried out his programme very carefully. He gives the source, preparation, properties, tests, and application of seventy-six indicators and seventy-four test-papers, arranged alphabetically in two divisions. In compiling the book the author has examined chemical journals and reports of societies in five languages.

Chemists employing volumetric methods will find this a useful book for reference.

H. C. B.

CHEMICAL NOTICES FROM FOREIGN SOURCES

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxi., No. 8.

Some Criticisms on M. Raoult's Cryoscopic Measurements.—A. Ponsot.—A controversial paper, not suitable for abstraction.

Method of Determining Molecular Weights, based on the Measurement of the Tension of Dissociation of the Hydrates of Gases.—G. Rosset.—Instead of measuring vapour-tensions, always very small in the case of aqueous solutions, the author endeavours to deduce them from the measurements of the tensions of dissociation of gaseous hydrates; these being much greater, enable measurements of relatively greater precision to be made. At 0°, for example, the dissociation tension of hydrate of chlorine varies 40 m.m. for a change of 0.1 m.m. in the vapour-tension of the aqueous solution, on contact with which it is dissociated. The method in question consists of measuring the dissociation-tension of a suitable gaseous hydrate in contact with an aqueous solution containing a known weight of a substance of which we wish to find the molecular weight, and to imitate this tension with the corresponding tension in the presence of pure water.

On Glycerophosphoric Acid.—J. Cavalier and M. Pouget.—According to Pelouze, the alkaline-earthly

glycerophosphates are less soluble hot than cold. The authors have measured the solubility of glycerophosphate of lime in water at different temperatures, and obtained the following results:—

100 grms. of solution contained at—	Anhydrous glycerophosphate of lime.
16°	7.9 grms.
36°	4.4 "
51°	2.3 "
77°	1.3 "
86°	1.25 "
100°	1.15 "

Consequently, a cold saturated solution deposits the greater part of its salt on boiling, retaining only one-eighth part. Glycerophosphate of barium behaves in a somewhat different manner; its solutions being more easily decomposed by heat, and the precipitation by heat is less abundant. The authors have also estimated the speed of decomposition of glycerophosphoric acid by water at a temperature of 88°, and they found that it has less stability than the ethylic compound, but about the same as the methylic and allylic ethers.

Action of the Hydrazines on the Chloranilic and Bromanilic Acids.—A. Descomps.—The author has already announced the preparation of a compound which takes place when one molecule of chloranilic acid, dissolved in alcohol at 80°, is treated with two molecules of phenylhydrazine. Continuing his research, he has acted with phenylhydrazine on bromanilic acid under the same conditions. A voluminous pale red precipitate is immediately formed answering to the formula $C_6O_2Br_2 < \begin{matrix} OH-C_6H_5NH-NH_2 \\ OH-C_6H_5NH-NH_2 \end{matrix}$. This compound, designated by the letter α , is susceptible, like the α -derivative of chloranilic acid, of being transformed under the influence of alcohol at 90° into an isomeric β -derivative, crystallised in prisms of an intense violet-brown colour; but the transformation, which was complete with the chloranilic acid derivative, is in this case only partial.

MISCELLANEOUS

The Paris Exhibition.—Mr. C. Wilkes, 29, Ludgate Hill, London, has been appointed General Manager and Sole Agent for the British Empire (Canada excepted) for all English advertisements or publicity in the General Official Catalogue of the Paris 1900 Universal Exhibition; also for the French and English Guides and other publications issued by Messrs. Lemerrier and Co., Official Contractors to the French Government and Exhibition Board.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

"Nitragin" and Soil Ferments.—I should feel much obliged if any of your correspondents will inform me of any publications, books or pamphlets, or Society's papers or lectures, which touch at all upon (1) soil ferments, (2) "nitragin," which may have appeared during the last three years, or anything connected with microscopic life (late advances) in the soil.—HOWARD B. EVANS.

MEETINGS FOR THE WEEK.

MONDAY, 6th.—Royal Institution, 5. General Monthly Meeting.
— Society of Chemical Industry, 8. "On 'Velvirl' Material, a new Substitute for India-rubber and Gutta-percha," by Walter F. Reid, F.I.C., F.C.S.
WEDNESDAY, 8th.—Geological.
FRIDAY, 27th.—Physical, 5. (At Central Technical College, South Kensington). "Contact Electricity," by F. S. Spiers. "Heat of Formation of Alloys," by J. B. Tayler.

To CHEMICAL MANUFACTURERS, CAPITALISTS and Others.

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October, 1899.

THE CHEMICAL NEWS.

VOL. LXXX., No. 2085.

THE PRESENCE OF POTASSIUM NITRITE IN BROWN POWDER RESIDUE WHEN THE POWDER IS BURNT IN AIR UNDER ORDINARY PRESSURE.

By Lieut. SETON, R.A., and Lieut. STEVENSON, R.A.

ORDINARY black powders when burnt in air under ordinary pressure leave a small quantity of residue in which carbonate, sulphate, and sulphide of potassium predominate. Traces only of nitrate and nitrite and other components can usually be found. When examined quantitatively, however, the three salts above mentioned together make up some 98 per cent of the whole. Brown powders burn much more slowly, and in consequence the residue is larger. It is generally white or greyish-white, hygroscopic, and for the most part soluble in water.

Some analyses were made of these brown powder residues to determine the relation of sulphate to carbonate. No sulphide is as a rule present. It was first noticed on acidifying that red fumes were produced. This of course indicated presence of nitrites in more than mere traces.

Several determinations of the amount of nitrite, by permanganate and by the nitrometer, gave about 6 per cent calculated as KNO_2 .

The figures of one complete analysis of residue from a brown powder are:—

K_2CO_3	61.96
K_2SO_4	26.18
KNO_2	6.17
Silica and other substances insoluble in H_2O	5.8
						100.11

Ordnance College, Woolwich.

ON THE SOLUTION OF AN IRON ANODE IN A SOLUTION OF ACETATE OF SODIUM AND ACETIC ACID.

By G. ARTH.

It has been well known since Renault's experiments on batteries (*Ann. Chim. Phys.*, 1867, vol. ii., p. 137) that an iron electrode dissolving in the circuit formed on itself always dissolves in the bivalent state whatever the electrolyte used may be, even when composed of oxidising liquids, such as a solution of chlorate of potash containing hydrochloric acid, or even dilute aqua regia. Round the anode there forms a blue zone if a drop of ferricyanide of potassium be carefully added, which indicates the presence of a ferrous salt; this reaction cannot, however, be obtained beyond a certain distance from the electrode on account of the oxidising action of the solution used.

It appears that this reaction does not always take place—at least, not under special conditions, and when the iron anode is submitted to the action of a current produced outside the cell in which it is dissolved. The following is the arrangement adopted for the experiments, which gave different results:—

A strip of iron, as pure as possible, 50 m.m. long by 12 to 15 m.m. wide and about 2 m.m. thick, was suspended by a platinum wire in the centre of a platinum cylinder of the same height and about 35 m.m. diameter. The whole was plunged in a jar of 15 c.m. high, filled with a solution of acetate of sodium containing acetic acid

(generally 50 grms. of crystallised acetate and 50 grms. of glacial acid per litre). The strip of iron is connected with the positive pole and the platinum cylinder with the negative pole of an accumulator battery. An ammeter and a rheostat must be placed in circuit, and a voltmeter connected to the terminals of the cell.

a. In this solution the strip of iron only dissolves, naturally, to a very slight extent; but as soon as the circuit is closed, even when only a very small current at a low voltage is passed, the solution of the iron commences at once. The salt produced forms colourless striæ, which are easily seen below the strip of iron, and the disengagement of gas is hardly perceptible at the surface of the metal, while bubbles of hydrogen appear immediately on the platinum cylinder. The phenomenon remains thus so long as the current does not exceed certain limits. It is easy to make certain that during this period the iron dissolves in the bivalent state, as in Renault's experiments, and that only ferrous acetate is formed. The liquid, in fact, remains colourless, the yellow prussiate does not give any Prussian blue, and if a silver voltmeter is placed in the circuit we find the atomic relation $\frac{1}{2}\text{Fe} = \frac{28}{107.93}$ almost theoretically correct between the weight of silver deposited and the weight of iron dissolved.

No.	Volts.	Ampères.	Fe dissolved.	Ag de- posited.	Time. h. m.	Relation.
I.	0.79—0.92	0.17—0.10	0.2275	0.8645	2 —	$\frac{28.40}{107.93}$
II.	1.05—1.35	0.36—0.25	0.4894	1.8736	1 45	$\frac{28.19}{107.93}$

b. If the current traversing the cell is more intense, the phenomenon is quite different. I have observed two cases which it is necessary to mention. At a certain moment the strip of iron became polarised, the needle of the voltmeter goes up while that of the ammeter goes down; the iron generally becomes covered with a reddish zone of liquid, which disappears after a few moments, at the same time that gas comes off abundantly from the surface of the metal. In this case the iron strip may become almost passive (especially if it is polished), as the results of the two following experiments show:—

No.	Volts.	Ampères.	Fe dissolved.	Ag de- posited.	Time. h. m.	Relation.
I.	2.93—3.50	0.31—0.38	0.023	1.080	— 50	$\frac{2.29}{107.93}$
II.	3.20—3.36	0.34—0.41	0.0195	1.6725	1 10	$\frac{1.25}{107.93}$

The small amount of iron dissolved is always found in the ferric state.

c. In other experiments, after the polarisation of the iron, a very small quantity of gas only is given off at the surface of the iron, and the sharp red striæ are seen below, caused by the formation of ferric acetate; the colour of the liquid and the reaction with ferrocyanide of potassium indicate the formation of a salt with the maximum quantity of iron. If we now place a silver voltmeter in the circuit we obtain the following results:—

No.	Volts.	Ampères.	Fe dissolved.	Ag de- posited.	Time. h. m.	Relation.
I.	2.24—2.41	0.11—0.05	0.0844	0.4532	2 15	$\frac{20.09}{107.93}$
II.	2.70—2.80	0.2	0.5618	3.1547	4 20	$\frac{19.21}{107.93}$
III.	2.80—3.07	0.24—0.19	0.3907	2.0016	2 45	$\frac{21.06}{107.93}$
IV.	3.20—3.30	0.42—0.28	0.1693	0.9505	— 50	$\frac{19.22}{107.93}$
V.	3.53—3.60	0.41—0.32	0.4586	2.5910	2 5	$\frac{19.10}{107.93}$

Theoretically, the relation is $\frac{\frac{1}{2} \text{Fe}}{\text{Ag}} = \frac{18.66}{107.93}$. In spite of the disengagement of a small quantity of gas, the figures obtained in these experiments are always a little higher than the theoretical value 18.66; a certain portion of the iron must therefore be dissolved in the bivalent state, and, as a matter of fact, ferricyanide of potassium always gives a blue precipitate in the liquid close to the iron. However this may be, the relations found seem to prove that ferric acetate is formed directly by the solution of the iron in the trivalent state, and not by the subsequent oxidation of the ferrous acetate first formed. Further, one can see no reason why ferrous acetate should be oxidised in this series of experiments, as in the first series it is not oxidised in an identical solution.

With regard to these phenomena, we must not forget the experiments and the theory of Wohlwill on the ions of tri- and mono-valent gold (*Zeit. fur Elektrochemie*, iv., pp. 379, 402, 421). I have not yet been able to determine exactly how and at what moment these changes take place. The phenomenon appears to be very complex, and depends on a considerable number of factors. I propose, however, to continue the research, using solutions of varied composition.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 16.

COMMERCIAL SEPARATION OF COPPER FROM THE ELECTRO-POSITIVE GROUP OF METALS

(NICKEL, COBALT, IRON, ZINC).

By B. NEUMANN.

IN the electrolytic refining of copper a certain number of metals contained in the anode (raw copper) pass directly into the slimes. These are:—Silver, gold, platinum, bismuth, tin, arsenic, antimony, and lead. Other metals are not precipitated from the solution, except by prolonged standing after saturation. The most electro-positive metals (nickel, cobalt, iron, and zinc) are dissolved from the anode at the same time as the copper, but are not deposited at the cathode on account of the low electro-motive force used. The bath, which is originally formed of an acid solution of sulphate of copper, thus gradually becomes enriched with metals of this group, and at the same time becomes poorer in copper. If the anode contains a much higher proportion of electro-positive metals than is generally found in raw copper, such as is the case with brass, old cartridge cases, German silver, &c., pure copper will still be deposited at the cathode so long as the electro-motive force used is not higher than that generally used in refining copper.

The problem the author has studied is the examination of the character of the electrolytic copper deposited at the cathode when working with baths charged more or less with electro-positive metals. The conclusions arrived at may be summed up in the following manner:—

Alloys of copper with the electro-positive metals, such as nickel, cobalt, iron, and zinc, can be refined in the ordinary manner. Copper alone is deposited at the cathode, the other metals remaining in solution. The electro-motive force should not exceed 0.5 volt for each bath. As the electrolysis progresses the resistance of the electrolyte increases on account of its loss of copper, and gains in foreign metals; the effective return from the current thus diminishes. Further, the quality of the copper deposited becomes less and less satisfactory, so that at a certain moment it becomes necessary to stop the operation.

The experiment of Foerster and Seidel has shown that the precipitation of the reddish brown pulverulent copper is caused by the occurrence of a certain concentration of the solution too weak in ions of copper. In the refining

of alloys of copper, therefore, a point is at last reached where only spongy copper is deposited. The addition of sulphuric acid in no way remedies this inconvenience, and, according to the law of the action of masses, such an addition would even tend to favour the formation of spongy copper. The only practicable method is therefore to withdraw the liquor and precipitate the copper from it by means of sulphuretted hydrogen, and to proceed with the electrolysis in a fresh sulphuric bath. The use of sulphuretted hydrogen to precipitate the rest of the copper is, further, more economical than the introduction of anodes, either insoluble or composed of electro-positive metals.

An Austrian company is at present refining raw copper containing 20 per cent of impurities. Under these conditions Canadian ores, which contain equal parts of copper and nickel, might easily become of much greater value than they now possess, owing to the difficulty of their treatment.—*Zeitschr. fur Elektrochemie*, vol. iv., pp. 316—322, and 333—338.

ON THE CAUSES OF EXPLOSION IN THE MANUFACTURE OF BRONZE POWDERS.

By M. STOCKMEIER.

SEVERAL explosions have been recorded in the last few years in factories where aluminium-bronze powder is ground. The author has made several experiments with a view to ascertaining under what conditions explosions are possible.

He has found that the powder itself is stable both to shock and while being ground. When mixed with chlorate of potash it detonates either when struck or by simply rubbing. It can also be detonated by means of an electric spark when shaken up in a vessel containing air. Aluminium-bronze is capable of decomposing water; the quantity of hydrogen produced varies under certain conditions, such as the nature and quantity of the grease always present. The bronze powder is hygroscopic, and, according to the author's experiments, it is capable, when dry, of absorbing up to 1.40 per cent of atmospheric moisture. Thus, in grinding up 5 or 6 kilogrms. of bronze powder, at 1.4 per cent of water, we can produce 43.4 to 52.08 litres of hydrogen. This hydrogen forms with air a detonating mixture which may be exploded by a spark produced by the passage of a small stone or other foreign body through the rollers.

The most effective method of preventing these explosions would be to replace the air which comes in contact with the powder by an inert gas, but unfortunately such a thing is quite impracticable.

All risk of explosions may, however, be avoided by observing the following precautions:—

1. The powder must be perfectly dry before being placed in the grinding machine.
2. The shop in which the grinding is carried on should be as nearly as possible kept at the same temperature as the machines in operation.
3. If the powder becomes brown during the grinding the machine must be stopped, the charge removed and placed in a cool place, and the machine carefully cleaned and aired.
4. The shop should also be well aired if the powder begins to show signs of attack during drying, or while being mixed in the receivers.
5. The Quirn-Schmidt apparatus should not be used, as it is not sufficiently safe.
6. The finished powder should not be packed in the grinding shop.
7. The grinding machines should be frequently examined.

8. The air should be kept as free as possible from aluminium dust.—*Zeits. f. Untersuch. Nahr. u. Genussmittel*, 1899, p. 49.

AQUEOUS SOLUTIONS OF METALLIC GOLD.

By R. ZSIGMONDY.

THE author gives a few details for the preparation of a red solution of *colloidal gold*. The following method gives good results:—25 c.c. of a solution of chloride of gold (hydrochlorate of chloride of gold) containing 0.6 gm. per litre, are diluted with 100—150 c.c. of distilled water, and 2 to 4 c.c. of a double decinormal solution (0.2 N) of carbonate or bicarbonate of potassium. The slightly alkaline solution thus obtained is boiled, the flame is then withdrawn, and 4 c.c. of a solution containing one part of recently distilled formic aldehyde (boiling-point 97—100°) in 100 parts of water, are carefully but rapidly added, the solution being continuously stirred all the while. The reaction is over in a few seconds, and the solution, colourless at first, takes a very brilliant red tint.

The success of the operation appears to depend on the purity of the distilled water used. Mere traces of phosphate will prevent the reaction. Very often the solution obtained has a violet or blue-black colour, and is not clear. It is impossible to prepare large quantities (2 or 3 litres) of the red solution at one time, on account of the difficulty experienced in adding the formic aldehyde sufficiently quickly.

Solutions prepared as described above, and containing 0.005 per cent of gold, can be boiled, or kept for several months without undergoing the slightest change. On submitting the solution to dialysis in a warm place (40—50°), foreign matters can be eliminated, and the proportion of gold present be brought up to 0.12 per cent.

The author then describes the properties of the solution of colloidal gold: he arrives at the conclusion that the gold is really dissolved in the water, and is not in the state of particles of metallic gold or oxide of gold in suspension in the liquid. Most acids and mineral salts re-precipitate the gold from this solution.

In 1857 Faraday prepared similar coloured liquids; but he expressed the opinion that the gold existed in the state of extremely finely divided metallic particles.

The author is examining the relationship existing between these auriferous liquids which he has prepared and purple of Cassius.—*Annalen*, cccl., [1], p. 29.

ON THE PURIFICATION OF IRIDIUM.

By E. LEIDIE.

WHEN we purify commercial iridium by Sainte-Claire Deville and Debray's method (fusion of the metal with lead, and subsequently attacking the ingot with nitric acid and aqua regia), we obtain a residue which should contain only iridium, ruthenium, and a little iron; but if the proportion of rhodium to be removed is too great, if the iridium is obtained from osmides not quite free from osmium, and if the attack of the metal by lead and that of the ingot by the acids has been incomplete, then the residue further contains rhodium, osmium, lead, and sometimes gold.

The originators of the method have mentioned these facts, and have further described a method which enables us to separate the foreign metals from iridium, but their process necessitates the use of a series of long and delicate operations.

The following method, which is specially applicable to the separation of the above-mentioned metals from iridium, is based on their transformation into chlorides,

and on the systematic use of nitrite of sodium; the following is a *resumé* of the method:—

I. The iridium, finely powdered and mixed with double its weight of melted chloride of sodium, is heated in a current of dry chlorine at a dull red heat; all the metals are thus transformed either into chlorides or double chlorides. The cooled mass is treated with about twenty-five or thirty times the weight of metal used, of water slightly acidulated with hydrochloric acid; it is then filtered; all the metals are in solution in the state of chlorides.

II. This solution is heated to about 50—60°, and small quantities of nitrite of sodium are progressively added until nitrous fumes are no longer given off and it has become neutral to litmus. Carbonate of sodium is then added until the solution is distinctly alkaline, when a fresh quantity of nitrite of sodium is added; this must be done very carefully, on account of the disengagement of gas if osmium is present; it is then boiled for a few moments and filtered. Under the influence exercised by nitrite of sodium under these conditions, that is to say, in a medium first neutral and then alkaline, the iron and lead in the form of oxides, and the gold in the metallic state, have been precipitated and remain on the filter; the chloride of osmium is transformed into osmate of sodium, OsO_4Na_2 , and the chlorides of ruthenium, rhodium, and iridium into the corresponding double nitrites, $\text{Ru}_2(\text{NO}_2)_4 \cdot 4\text{NO}_2\text{Na}$, $\text{Rh}_2(\text{NO}_2)_6 \cdot 6\text{NO}_2\text{Na}$, and $\text{Ir}_2(\text{NO}_2)_6 \cdot 6\text{NO}_2\text{Na}$,—all four soluble in water.

III. To this solution an excess of soda is added, and a current of chlorine is passed through, first in the cold, and afterwards while heating gradually up to 50—60°; the alkaline hypochlorite formed causes the osmium and ruthenium to pass to the state of peroxide of osmium, OsO_4 , and peroxide of ruthenium, RuO_4 , which distil under the influence of heat; care must be taken that the apparatus used for distillation should be formed entirely of glass. These peroxides are collected first in a tube plunged in ice, and then in a flask containing potash.

IV. The solution contains only nitrites of rhodium and iridium, with the alkaline chlorate and nitrate formed during the course of the operation. By acidulating this solution with hydrochloric acid, evaporating to dryness, and once more repeating the reaction with acid and evaporating, a saline residue may be obtained containing only chloride of sodium, with the double chloride of rhodium, $\text{Rh}_2\text{Cl}_6 \cdot 6\text{NaCl}$, and the chloroiridate, $\text{IrCl}_4 \cdot 2\text{NaCl}$; this residue is taken up with cold chlorine-water, the solution is set to crystallise so as to separate the greater part of the chloride of sodium which is first deposited. The crystals which form last are a mixture of the two above-mentioned chlorides, $\text{Rh}_2\text{Cl}_6 \cdot 6\text{NaCl}$ and $\text{IrCl}_4 \cdot 2\text{NaCl}$. These crystals are drained and thoroughly dried at 105°, after which they are heated for four hours at 440° (in a sulphur vapour oven) in an apparatus traversed by a current of dry chlorine; the mass is allowed to cool in a current of chlorine and then treated with cold chlorine-water. The double chloride of rhodium is transformed into a mixture of chloride of sodium soluble in water, and insoluble sesquichloride, Rh_2Cl_6 , like that prepared at a high temperature in the dry way; as to the chloroiridate it remains unchanged, the Rh_2Cl_6 is separated by filtration.

V. The filtrate contains only chloride of sodium and chloroiridate of sodium; the latter, by the addition of a large excess of chloride of ammonium, is precipitated in the form of chloroiridate, $\text{IrCl}_4 \cdot 2\text{NH}_4\text{Cl}$, insoluble in a saturated solution of sal-ammoniac; it is thrown on a filter, and washed with a saturated solution of sal-ammoniac to remove all the chloride of sodium. There now only remains to dry the chloroiridate of ammonium, and to decompose it by heating to dull red in a current of hydrogen, and allowing it to cool in a current of dry carbonic acid. Thus we obtain pure iridium.

To succeed in the separation of rhodium from iridium

it is necessary to observe two indispensable precautions :
a. An excess of chloride of sodium should be guarded against; this substance, in fact, gives stability to the double chloride, $\text{Rh}_2\text{Cl}_6, 6\text{NaCl}$, which can be maintained in an unaltered state in a mass of melted chloride of sodium; the rhodium salt should therefore be dissolved with that of iridium.

b. The chlorine must be perfectly dry; in fact, at 440° in the presence of water vapour it gives rise to the formation of hydrochloric acid, and the chloroiridate heated in this gas at 440° decomposes into chlorine and sesquichloride, Ir_2Cl_6 , of which a part would pass into solution with the rest of the iridium in the form of the double chloride, $\text{Ir}_2\text{Cl}_6, 6\text{NaCl}$, but the other part of which would remain with the rhodium in the form of the sesquichloride, Ir_2Cl_6 , insoluble in water.

This method, the application of which to a particular case I have just described, may be generalised.

I propose shortly to publish its application to the general case of the separation of the metals of the platinum group, one from the other, by the wet method.—*Journ. de Pharm. et de Chim.*, Series 6, vol. x., No. 4.

ON A CHLORO-IODIDE OF TIN.

By C. LENORMAND.

In a previous paper (*Journ. de Pharm.*, 13 Sept., 1898), I described the conditions under which a new compound, SnCl_2I_2 , is produced. I also showed that when distilled in air it left a residue of SnI_4 , and gave as distillate a liquor in which tin was found, as well as chlorine and iodine, in undefined proportions, but which contained all the chlorine contained in the original product. I showed that this liquor, when distilled several times, allowed a quantity of iodine decreasing successively to pass, and at the fifth distillation in air, nothing but bichloride of tin passed over. I then showed that the final decomposition of SnCl_2I_2 ought to take place according to the following formula, $2(\text{SnCl}_2\text{I}_2) = \text{SnCl}_4 + \text{SnI}_4$.

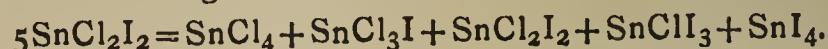
At the end of the paper I remarked:—"The decomposition of SnCl_2I_2 takes place according to the preceding formula; but according to what formula do the first and succeeding distillations take place? Stannic iodide forms the residue at each distillation; now this body is not volatile at the temperatures at which I worked; how therefore does the iodine pass over on distillation? Must we admit the formation of an intermediate volatile chloro-iodide of tin?"

Since then I have taken up this subject again; but instead of carrying on the distillation in the ordinary manner, I did it in a fractional distillation apparatus; at 126° a red coloured liquid came over, then the temperature gradually rose until it reached 180° , where it appeared to stop. But on prolonging the heating it finally reached 280° , where it stopped definitely; at precisely this moment a phenomenon occurred which I had never noticed before on account of the form of my first apparatus; the escape tube became filled with an orange-red crystalline product. On analysis this body showed the composition of a chloro-iodide, SnClI_3 .

The liquid distilled between 126° and 180° , rectified, not in air this time, but in vacuo, allows another liquid to pass between 28° and 30° , the composition of which shows it to be stannic chloride, and leaves a residue the composition of which varies with the duration of the rectification. In fact, if this be stopped when the distillate is about two-thirds of the original volume, the residue has the formula of a chloro-iodide, SnCl_3I ; if, on the contrary, instead of stopping the distillation at this moment, it is allowed to go on longer, the composition of the residue is that of a chloro-iodide of tin, SnCl_2I_2 .

According to these observations, the decomposition, by

heat, of the chloro-iodide, SnCl_2I_2 , takes place according to the following formula—



The liquid distilled in air thus consists of (1) stannic chloride; (2) the chloro-iodide, SnCl_3I ; (3) part of the original chloro-iodide, SnCl_2I_2 ; (4) the chloro-iodide of tin, SnClI_3 .

The chloro-iodide of tin, SnCl_2I_2 , distilled direct in vacuo, behaves in a much more simple manner; there are no intermediate compounds formed, but we at once obtain, under a pressure of a few m.m.:—

1. Stannic chloride which distils over;
2. Stannic iodide which remains as the residue.

The direct decomposition of this compound in vacuo is therefore represented by the formula—



On a Bromo-iodide of Tin.—Iodine in the cold is without action on protobromide of tin, but when we use, as I did, a closed vessel at 100° , an energetic reaction takes place; the mass becomes liquid and the iodine disappears in the proportion of 254 grms. of this body for 278 grms. of protobromide of tin.

The new compound, liquid at 100° , is not so at the ordinary temperature; it is then solid and occurs as a crystallised reddish-orange mass.

After careful decantation at 100° it gave on analysis the following results:—

	Calculated. SnBr_2I_2 .	Found.		
Tin ..	22.18	22.38	22.31	22.23
Bromine ..	30.08	29.56	29.62	29.60
Iodine ..	47.74	47.19	47.54	47.68
	100.00	99.13	99.47	99.51

Its composition therefore corresponds to that of a bromo-iodide of tin, SnBr_2I_2 .

I estimated the bromine and iodine by Rose's method, and the tin by the method I have previously described.

This new compound is solid at the ordinary temperature, it is orange-red in colour, and crystallises in hexagonal tables. At 50° it commences to melt, when liquid it has a beautiful ruby colour. In this state it gives off very little fumes, and when cold none at all. Its density taken at 15° equals 3.631. When placed in water it is difficultly soluble in the cold; on raising the temperature it dissolves rapidly. Towards 80° its aqueous solution decomposes into insoluble hydrate of oxide of tin, and into hydrobromic and hydriodic acids which remain dissolved.

When submitted to the action of heat in a fractional distillation apparatus, it begins to melt at 50° , and boils at 225° .

Between 230° and 250° a product is distilled over which crystallises in orange-yellow crystals in the escape tube; the formula of this body is that of a bromo-iodide, SnBr_3I .

Between 250° and 275° a product is collected which again crystallises in the escape tube; its composition is that of the original bromo-iodide, SnBr_2I_2 .

Finally, at this moment there remains in the flask an orange-red compound, having the composition of the bromo-iodide, SnBrI_3 .

According to these observations the decomposition in air of the bromo-iodide, SnBr_2I_2 , may be represented by the formula $3\text{SnBr}_2\text{I}_2 = \text{SnBr}_3\text{I} + \text{SnBr}_2\text{I}_2 + \text{SnBrI}_3$.

When distilled in vacuo the bromo-iodide, SnBr_2I_2 , boils at 130° , and distils a little above this point; the temperature increases gradually and reaches 180° , at which point it remains. At this moment the product distilled has the composition of a bromo-iodide, SnBr_3I , and the residue that of another bromo-iodide, SnBrI_3 .

Thus the decomposition in vacuo of the bromo-iodide, SnBr_2I_2 , is not effected like that of the chloro-iodide

SnCl_2I_2 , since the formula which expresses its decomposition is the following, $2\text{SnBrI}_2 = \text{SnBr}_3\text{I} + \text{SnBrI}_3$.—*Journ. de Pharm. et de Chim.*, Series 6, vol. x., No. 3.

ELECTROMOTIVE PROPERTIES OF CHROMIUM: ACTIVE AND PASSIVE CHROMIUM.

By W. HITTORF.

IN a paper presented to the German Electro-chemical Society, the author describes the results of some experiments made with two samples of metallic chromium prepared according to Goldschmidt's process.

According to Wöhler zinc precipitates metallic chromium from its melted salts; we might therefore conclude that chromium would immediately follow zinc at the positive end of the electromotive series of metals. It has, however, been found that when chromium is plunged into certain solutions, such as dilute hydrochloric acid, which do not cause a disengagement of hydrogen at the ordinary temperature, not only is it electro-negative with regard to zinc, but also to cadmium, iron, nickel, copper, mercury, and silver. It is without action on the neutral salts of these metals even when boiling. The chlorides of gold, palladium, and platinum are also unattacked. Only the bichlorides of mercury and copper and cupric bromide are reduced to the state of mercurous and cuprous salts at boiling point. From this point of view chromium behaves therefore like silver; but at a low temperature it behaves generally like a noble metal.

It must be remarked that chromium forms three kinds of compounds corresponding to the three degrees of oxidation, CrO , Cr_2O_3 , CrO_3 , and that when we use it as an anode for the electrolysis of a single electrolyte, ZnCl_2 , it dissolves, forming different compounds according to the temperature, and according to the nature of the solvent used.

Chromium exists in three distinct states, *passive*, *active*, and *indifferent*; under each of these forms it occupies a different position in the electromotive series of metals, and possesses different chemical properties.

In the *passive* state it is a noble metal. It has no reducing action on the salts of other metals, and follows platinum at the end (electro-negative) of the electromotive series of metals. This is its normal condition at the ordinary temperature, and when it is used as an anode in the electrolysis of chloride of zinc, chloride of sodium, hydrochloric acid, &c., it dissolves, forming chromic acid, which colours the solution in the neighbourhood of the anode yellow.

In the *active* state, which is generally manifest at higher temperatures, it immediately follows zinc in the voltaic series, and displaces all the more electro-negative metals from their solutions.

Used as an anode in the electrolysis of the chlorides at boiling point, it dissolves in the state of protochloride, CrCl_2 , colouring the solution a bluish green. In certain cases it is necessary to heat the solution to above 100° , as, for example, when we electrolyse the chlorides of magnesium or zinc. An anode of chromium remains passive in a dilute boiling solution of chloride of zinc containing an excess of oxide of zinc to neutralise all trace of hydrochloric acid, and we notice the yellow colouration of chromic acid. If, on the contrary, the solution is slowly evaporated the temperature rises gradually to about 130° on account of the concentration, and at this temperature we notice the green colour due to protochloride of chromium, CrCl_2 . The passage of chromium from the inactive or passive state to the active state is again placed in evidence by the following experiment.

Passive chromium can be kept for no matter how long a time in solutions of chloride of copper, gold, palladium, or platinum without reducing them. But if we place it in a boiling solution of chloride of potassium or sodium it

immediately passes to the active state. Consequently, a fragment of chromium which, being used as an anode, has given chromic acid by electrolysis can be kept as long as is wished in a boiling solution of a chloride of a noble metal without there being a trace of reduction. But if we add an alkaline chloride reduction immediately takes place. This action is the more feeble as the quantity of alkaline chloride added is itself small. Further, it only takes place at a high temperature, and ceases as soon as the solution is allowed to become cold.

In the *intermediate* or *indifferent* state chromium occupies an intermediate position in the electromotive series and forms a compound which is also intermediate. The electrolysis of an alcoholic solution of chloride of zinc furnishes a green solution of CrCl_3 at the point of contact with the chromium anode.

Passive chromium does not combine with iodine, even in the nascent state, while the active modifications displace the iodine from hydriodic acid.

The author has also studied the action of chromium on the melted metallic salts. He admits that the passive state of iron can be explained by the formation of an invisible layer of oxide which protects the metal against any outside attack, but a similar explanation cannot be admitted in the case of chromium, as experiments have shown that such is not the case.

Finally, up to the present, no acceptable theory has been offered concerning these curious properties of chromium. In its several states this metal possesses properties so different, that one is almost tempted to attribute them to distinct metals rather than to one only.—*Zeitschr. für Elektrochemie*, 1898, iv. [21], p. 481.

PHOTO-CRYSTALLISATION.*

By FERDINAND G. WIECHMANN, Ph.D.

(Continued from p. 217).

INSPECTION of Table IV., which is self-explanatory, shows the following effects of exposure to light. All specimens in Series I. (exposed to direct sunlight) which crystallised completely, had attained to complete crystallisation long before any specimen in either of the other two series had reached this condition.

Thus, between the times of complete crystallisation of No. 1, Series I., and No. 10, Series II., the first of Series II. to crystallise wholly, there elapsed 484 days. Between the complete crystallisation of No. 1, Series I., and No. 14, Series III., the first of this series to crystallise completely, lies a period of 964 days.

All three series of specimens were kept in the same room throughout the entire time over which observation extended. Series II. and III. were therefore practically under identical temperature conditions. Series I., however, being exposed to direct sunlight undoubtedly received more heat-energy than the other series. Experiments in which this disturbing factor will be eliminated, by filtering the sunlight through a concentrated solution of alum before it reaches the sucrose solutions, are contemplated.

From these data it appears that, *cæteris paribus*, photo-crystallisation is directly proportionate to the intensity of illumination.

Nine specimens when taken for analysis were wholly crystallised. This is 50 per cent of the total number. These had turned solid in the following sequence and time (see Table V.).

In Series I. five out of the six specimens had crystallised completely, and it will be of interest to learn what relation the sequence of crystallisation bears to the composition of the specimens and the conditions to which they were subjected.

TABLE IV.

Number of sample.	Description of sample.		Condition of exposure.	Time, in days from beginning of experiment to—			Condition when analysed.
	Per cent invert.	Condition.		Appearance of first crystal.	Complete crystallisation.	Analysis.	
1.	90.9	Acid	Direct sunlight	25	127	273	Solid.
2.	90.9	Neutral	" "	25	281	333	"
3.	80.6	Acid	" "	25	225	273	"
4.	80.6	Neutral	" "	25	324	333	"
5.	58.0	Acid	" "	63	350	488	"
6.	58.0	Neutral	" "	99	—	1474	Semi solid.
7.	90.9	Acid	Diffuse daylight	25	1096	1114	Solid.
8.	90.9	Neutral	" "	25	—	859	Very nearly solid.
9.	80.6	Acid	" "	—	—	1475	Nine-tenths solid.
10.	80.6	Neutral	" "	—	611	810	Solid.
11.	58.0	Acid	" "	—	692	810	"
12.	58.0	Neutral	" "	170	—	1476	Semi-solid.
13.	90.9	Acid	Darkness	25	—	1484	Half solid; liquid amber colour.
14.	90.9	Neutral	"	25	1091	1115	Solid.
15.	80.6	Acid	"	25	—	1485	Nearly solid.
16.	80.6	Neutral	"	25	—	1488	Nine-tenths solid; pale amber liquid.
17.	58.0	Acid	"	—	—	1478	Very nearly solid.
18.	58.0	Neutral	"	365	—	1477	A few crystals in bottom; liquid amber colour.

TABLE V.

Number of specimen.	Time in days.
1	127
3	225
2	281
4	324
5	350
10	611
11	692
14	1091
7	1096

From inspection it appears that the acid solutions crystallised earlier than the neutralised solutions of the same composition. Thus, the specimen containing—

90.9 per cent invert-sugar, acid, crystallised in 127 days.	
90.9 " " neutral, " 281 "	
80.6 " " acid, " 225 "	
80.6 " " neutral, " 324 "	
58.0 " " acid, " 350 "	
58.0 " " neutral, did not crystallise.	

Furthermore it appears that of these three acid solutions, the one containing the highest percentage amount of invert-sugar, 90.9, was the first one to crystallise; next in order of crystallisation was the specimen containing 80.6 per cent of invert-sugar; while the one lowest in invert-sugar, 58.0 per cent, was the last to crystallise.

To summarise, it appears that photo-crystallisation of partially inverted sucrose solutions, under conditions as here studied, progresses most rapidly the stronger the light to which the solutions are exposed and the greater the amount of invert-sugar which they contain.

When these three series of solutions were originally prepared the amount of inverted sucrose in the same was determined in the usual manner, as invert-sugar, by Fehling's solution. However, after completion of the work thus far described, it appeared desirable to submit all of the specimens to a more exact analysis in order to learn more about their constitution.

Accordingly the sucrose, dextrose and levulose were, in each instance, individually determined. The author's method employed is here re-published (from the *School of Mines Quarterly*, xiii., No. 3); the $[\alpha]_D$ value of levulose is taken as -93.8 .

The Method.

Preparation of Solution.—If not already in solution, make of the sample to be examined a solution of arbitrary density. Of course, it goes without saying that this method is to be applied only in cases where no other optically active substances are present besides sucrose, dextrose, and levulose, and that care must be exercised that no preliminary treatment of the solution shall influence its original power of rotation.

The specific gravity of the solution above referred to is accurately determined by balance, and from this value there are calculated, in the following manner, the number of grms. of solution which contain 10.000 grms. of dry substance :*

Ascertain the degree Brix corresponding to the specific gravity found. Divide 100 by the degree Brix; the quotient represents the number of grms. of solution which contain 1.00 gm. of dry substance. This value is multiplied by 10, and the product represents the number of grms. of solution, equivalent to 10.000 grms. of dry substance.

This amount is weighed out, placed in an accurately graduated 100 c.c. flask, and the solution in the flask is made up to 100 c.c. with distilled water.

The determinations to be made are as follows :—

Optical Examination.—Some of the solution is placed in a water-jacketed polarisation-tube, a thermometer is inserted in the solution, and a reading on this solution is taken in the polariscope, at the temperature of 20° C.

The reading thus obtained must be reduced to the basis of a reading made in a 100 m.m. tube.

Furthermore, if a sugar-polariscope has been used for the observation, the reading obtained must be transformed into circular degrees. With a polariscope using 26.048 grms. as the normal weight, the factor 0.346 is used for the sodium ray.

Gravimetric Determination before Inversion.—Of the 10 per cent solution weigh out an amount equivalent to 1.0 gm. of dry substance. Make this up to 150 c.c., and of this solution take 24.4 c.c., equivalent to 0.1628 gm. dry

* This concentration is chosen because the specific rotary powers of the sugars, values needed in the calculation of results, vary with the concentration.

substance. Take 50 c.c. of Fehling's solution,* heat to boiling; while boiling add the 24.4 c.c. of sugar solution, and boil for three minutes.

Then remove from flame, add cold distilled water, previously boiled, in order to cool the solution and prevent a further deposition of cuprous oxide.

Filter through a weighed asbestos filter, wash, first with boiling water, then with absolute ethyl alcohol, and finally with ether. Dry perfectly, cool, and weigh.

Calculate the cuprous oxide to its equivalent of metallic copper, and from the copper thus found ascertain the amount of sucrose corresponding.† From this figure the total reducing-sugars by adding 1/20 to the sucrose value indicated.

Gravimetric Determination after Inversion.—Of the original 10 per cent solution, weigh off an amount equal to 5.000 grms. dry substance; invert with 4 c.c. of concentrated HCl (specific gravity 1.20) by heating on boiling water-bath up to a temperature of 67° C. and maintaining the solution at that temperature for five minutes. Then remove the flask, cool it and its contents to the temperature at which the flask was graduated, and then make the solution up to 100 c.c.

Of the solution thus obtained take 20 c.c. and neutralise with sodium carbonate; then make up to a volume of 150 c.c. with distilled water; of this solution take 24.4 c.c., equivalent to 0.1628 gm. of dry substance, and proceed precisely as previously directed. Determine the value found, as before, from the table; the result obtained represents the total sugars present, *expressed as sucrose*. From this amount subtract the sucrose value found by prior determination,‡ and the difference represents the amount of sucrose actually present.

The results thus obtained represent:—the polarisation, in a 10 per cent solution, of the three sugars combined; the total reducing-sugars present; the amount of sucrose present.

In cases where the reducing-sugars—*i. e.*, the dextrose and the levulose together, exceed in amount the sucrose present, the gravimetric determinations before and after inversion should preferably be made according to E. Meissl's method for the determination of invert-sugar (*Zeitschrift des Vereines für Rübenzucker-industrie*, xxix., 1034, and E. Wein, *Tabellen zur Quantitativen Bestimmung der Zuckerarten*, Table No. IV).

(To be continued).

EVOLUTION OF CHEMISTRY IN THE LAST TWENTY YEARS.‡

By Dr. A. LADENBURG.

(Continued from p. 198).

TURNING now to subjects that concern us more immediately, we shall here first consider the progress that has been made in analytical chemistry by the application of electrolysis. The subject of electrolysis is a very old one, and so early as 1801 Cruickshank predicted that it would be turned to account in this way. It was qualitative analysis, however, that alone derived any benefit from it at first. Magnus afterwards drew attention to the fact that quantitative analysis—that is, the separation of the metals—must be possible by means of electrolysis; and experiments in the same direction were made, moreover, by Gibbs and by Luckow. Classen, Miller and Kiliani,

Smith, Vortmann, and others, afterwards introduced the manifold applications of electrolysis to quantitative analysis; and Classen devised the form of apparatus by which the experiments are generally carried out. The great importance of the electromotive force was first recognised by Triliani and Le Blanc.

The applications of electrolysis to metallurgy are probably still more important. After the researches of Davy, it was especially those of Bunsen (published by the latter partly alone and partly in conjunction with Matthiessen) that brought about any notable advancement. Electrolysis first found a technical application upon the discovery of electrotyping by Jacobi and Spencer in 1839, an art which depends, however, upon an observation made by De la Rive in 1836.

The technical production of metals by electrolysis only became possible after the discovery, in 1872, of the dynamo-electrical machine, which was employed immediately thereafter (in the North-German Refinery at Hamburg) to remove copper from solutions. Other metals, such as zinc, magnesium, lead, silver, gold, &c., were also produced electrically afterwards. An operation of outstanding importance was the electrolytic production of aluminium, a metal which Bunsen first prepared by this method. The technical process of Heroult is different, however, from that of Bunsen, inasmuch as it is not a fused double chloride of the metal that is electrolysed, but aluminium oxide.

This is the place to refer to the great scientific and practical results that Moissan obtained as the outcome of his experiments with the electric furnace. Specially worthy of mention in this connection are the preparation of artificial diamonds; the production of calcium carbide (which had, however, been discovered long before by Wöhler) and of many other carbides; the preparation, in a state of purity, of chromium and of other difficultly fusible metals, &c. The first preparation of carborundum, which is also frequently attributed to Moissan, is due rather to Acheson, an American. Attention must be drawn to the facts that in many of these experiments electricity is only employed as a means of attaining to high temperatures (3000° to 4000°), and that the results can also be obtained in other ways, since the same high temperatures can, of recent years, be reached by means of chemical reactions. An entirely new branch of thermo-industry has thus arisen, by means of which great advances have already been made, and are still to be expected, in metallurgy. Of an earlier date is the employment of the oxy-hydrogen blowpipe in the melting and working of platinum, and so is the combustion of carbon and other elements (such as silicon, sulphur, phosphorus, &c.) in air or oxygen at high temperatures, for the purpose of attaining still higher temperatures; as, for example, in the blast furnace, or in the ingenious Bessemer process. The development of these methods by Goldschmidt, and their application to the production of metals such as chromium, manganese, iron, and nickel, free from carbon, and of a large number of alloys, are new however.

I must here recall the interesting results obtained, partly by Victor Meyer and partly by Crafts, by the application of the method of vapour density determination devised by the former. I regard as worthy of mention the proof that the molecule of iodine, I₂, breaks up at high temperatures into single atoms; and also the facts that the beginning, at least, of a similar dissociation has been ascertained in the case of bromine; that the molecule of arsenic, As₄, similarly splits into two; that potassium iodide even at high temperatures corresponds to the formula KI, and cuprous chloride to the formula Cu₂Cl₂, &c.

If the attainment of high temperatures has thus been of service for the purposes of our science and of technology, so likewise the endeavours, on the other hand, to obtain low temperatures have led to great advances, and to results of altogether unforeseen importance. In a preceding lecture, where the inter-relations of the

* Cupric sulphate cryst., 34.639 grms. in 500 c.c. H₂O; Rochelle salts, 173.000 grms. in 400 c.c. H₂O; Sodid hydrate, 50.000 grms. in 100 c.c. H₂O.

† Table published by the German Government, Law of 1887; also in Weichmann, *Sugar Analysis*, Table XI.

‡ That is, the amount as actually found by Table, prior to the addition of 1/20.

§ Read before the British Association (Section B), Dover Meeting, 1899.

states of physical aggregation and the significance of the critical temperature are referred to, the results of Pictet, of Cailletet, and of Wroblewsky on the liquefaction of the so-called permanent gases are stated. Of special importance were the detailed investigations of Wroblewsky and Olszewsky, who first obtained quantities of oxygen and nitrogen in the liquid state, and particularly described many of their properties. The mode of measuring temperatures by determining the potential of thermo-electric currents, which is now largely employed, also originated with them. In the experiments that have been carried out latterly, however, on the liquefaction of air and of other gases, Pictet's method has been abandoned again, and recourse has been taken to that of Cailletet (the latter method having been converted into a dynamical or continuous one); that is to say, the expansion of highly compressed gases has been employed in order that the necessary lowering of temperature may be effected. Thus Dewar, in his experiments upon the production of liquid air, liquefied, by its own expansion, air which was under a pressure of 100 atmospheres and was cooled by solid carbonic anhydride; whereas the recent technical method consists in cooling exclusively by expansion, and the effect of the latter is turned to account in a very ingenious manner by the employment of a self-intensive apparatus. Linde in Germany, and Hampson in England, almost at the same time, constructed technically efficient forms of apparatus, based upon this method, for the production of liquid air.

Liquid air has not as yet, however, found any technical application upon the large scale. Nearly pure oxygen is obtained from it very cheaply, and the attempt has been made to apply it in the technology of explosives, or to the production of high temperatures, but no ultimate pronouncement can be made with respect to this. Of far greater importance are the results that liquid air has achieved from a scientific aspect.

In the first place it must be mentioned that Dewar, by its aid, has succeeded in liquefying helium, and in obtaining air, hydrogen, and oxygen in the solid state; and that in doing so he has achieved almost everything that can be done in this direction. Dewar is at present engaged in trying to reach still lower temperatures by the aid of liquid hydrogen boiling under low pressure, in order to approach as nearly as possible to the absolute zero.

It is also of importance that ozone, which was obtained in the liquid state by Hautefeuille and Chappuis in 1882, by the aid of liquid ethylene, can easily be prepared in an approximately pure condition by the use of liquid air, so that Troost was able to determine its boiling-point and Ladenburg its density. The latter determination is of especial importance, since the molecular formula O_3 , deduced from it, constitutes one of the most emphatic arguments in favour of the whole molecular theory; and this formula, which till then had only been supported by Soret's experiments, could not be regarded as finally settled.

But the results that have been furnished by this agency with respect to the discovery of new elements are of almost as great consequence.

When Lord Rayleigh compared the relative density of atmospheric nitrogen with that of nitrogen prepared from ammonia and other nitrogen compounds, he found a difference (in the third decimal place) which could not possibly be ascribed to an experimental error. He therefore resolved upon a minute investigation in order to find out the substance that was mixed with atmospheric nitrogen. This investigation he then carried out along with Ramsay, and it led to the discovery of argon, an element of which combinations are very difficult to be obtained. The molecular weight, deduced from the density, gave the number 39.92, and since, by Kundt's method, the monatomic character of the gaseous molecules was indicated, its atomic weight would be represented by the same number. The question as to the position of this

element in the Periodic System is thereby rendered an extremely difficult one, since it falls near that of potassium and yet is beyond it.

Ramsay took up the problem from a very general point of view. It appeared to him highly probable that argon was a member of a whole group of elements, of which group he hoped to find additional members associated with nitrogen. It was thus that he came to investigate, amongst other things, the gases evolved from clèveite by heating with sulphuric acid, which Hillebrandt had considered to be nitrogen, and this led him to the discovery of helium. The brightest line in the spectrum of this gas, D_3 (D_1 and D_2 are the sodium lines), had been observed a long time previously by Lockyer in the spectrum of the sun's photosphere. Helium, whose atomic weight 4 was deduced from the density of the gas and from the rate of propagation of sound in it, was an analogue of argon in every respect; and it was thus clear to Ramsay that there must be another element which, with atomic weight about 20, should be placed before sodium, in the same way that helium comes before lithium, and argon probably before potassium (although the atomic weight of argon has been found, in the mean time, somewhat higher than that of potassium). A similar thing applies to tellurium, the atomic weight of which, according to the most recent determinations, is greater than that of iodine.

Ramsay now represents the further development of the subject as if the investigation, carried out with his utmost energy and effort, had remained unproductive, and as if an accident only had led him on to his further discoveries. There is in reality, however, no such accident in question, for the investigation of the residue from the evaporation of liquid air was only a link in the chain which, although perhaps unknown to himself, represented the course of his ideas. In this way he discovered crypton, the molecular weight of which was ascertained in a preliminary manner to be 45. It should probably be much higher, however, as the gas was still mixed with lighter gases, especially with argon. In the case of crypton, the ratio of the specific heats has also been ascertained to be 1 to 1.66, so that this gas is also a monatomic element, the position of which in the Periodic System is still undetermined.

As regards other discoveries, Ramsay found, by the systematic fractionation of argon (which he condensed by means of liquid air), three new substances which he considers to be elements. These are—Neon, with atomic weight 19.3 to 19.5, which is clearly to be placed therefore between helium and argon and before sodium; xenon, with density 65 ($H=2$) which might, as Ramsay supposes, be raised to 81 by further purification, so that it would be placed beyond bromine; and, finally, metargon, an easily condensable and even solidifiable gas, which shows the spectrum of carbonic oxide even after it has been mixed with oxygen and exposed for a long time to the passage of electric spark.

Even although all doubt as to the individuality and the elementary nature of these gases is not yet removed, still these investigations are unquestionably amongst the most successful that have been carried out during the last twenty years. Liquid air served not merely as starting material for the investigations, but Ramsay also employed it, or at least the liquid oxygen obtained by its aid, in an ingenious manner for the purpose of separating the various new elements.

The question as to the position of these "elements" in the periodic system has been much discussed, and up to the present it is not finally solved. On the other hand, we may now say that even if our views respecting the connection between the properties of the elements and their atomic weights should be modified on account of these newly discovered facts, still the periodic law has rendered excellent service as an invaluable guide in this obscure region.

Although such unexpected discoveries were thus made, still they will not exercise any considerable influence upon

chemistry as a whole, since all these elements apparently resemble argon, and do, probably, not give many combinations. Hence it may be said that these interesting investigations will probably not prove of great significance as regards their consequences, and that in this respect they will fall short of other researches which have not excited the interest of such wide circles.

I merely recall here the isolation of fluorine by Moissan in 1886, the discovery of $\text{Ni}(\text{CO})_4$ and analogous compounds by Mond in 1890, and pass on to consider more particularly the investigation of the chemistry of nitrogen, which has made great advances in recent years.

The discovery of hydroxylamine, by Lossen, falls under review here, although, of course, it took place at a much earlier date (in 1865). It has not been referred to previously, however, since its importance only came to be recognised gradually, a result to which Victor Meyer's researches on the oximes and their stereo-isomerism materially contributed.

The preparation of phenylhydrazine, by Emil Fischer, also falls to be mentioned here. It must be looked upon as of outstanding importance, on account of its leading to the clearing up of the sugar group. Following upon this there are the valuable researches of Curtius, who discovered hydrazine in 1889 and hydrazoic acid in 1890. The utilisation of these two substances has already led to numerous investigations, and will lead to others. As worthy of mention I also refer to the researches of Thiele, who (amongst others) found out a convenient and technically practicable method for the manufacture of hydrazine; and to those of Raschig, who cleared up the nitrogen-sulphonic acids, and in doing so discovered the method now employed for the production of hydroxylamine.

It does not seem to me that this is the place to enter more fully into this subject, since I am really giving a historical sketch, in which only those things that are of general importance can be prominently brought forward.

I may thus recall here a discovery of Hellriegel's which marks an epoch in chemistry and agriculture. According to Hellriegel, leguminous plants, and lupins in particular, possess the power of assimilating, with the aid of lower organisms, the nitrogen of the air. In this connection the fact must not be passed by without mention that Berthelot had previously asserted the assimilation of free nitrogen.

An observation which is to a certain extent of an opposite character is the proof furnished by Buchner that fermentation is possible even without living organisms, by means of the liquid expressed from yeast (zymase).

More particular consideration may be given to a research by van't Hoff, in which the idea and the significance of the transition temperature are clearly stated. Van't Hoff is led to the idea by the comparison of chemical reactions with the transitions from one of the states of physical aggregation to the others; but the same conception may be arrived at by the aid of the phase rule.

(To be continued).

Compounds of Formic Aldehyde with Menthol and Borneol.—A. Brochet.—The formals obtained have the general form $\text{CH}_2(\text{OR})_2$. Dimentholic formal is a white solid body with a rather agreeable odour, insoluble in water, but very soluble in ether and benzene. It is hardly soluble in cold alcohol, but is miscible in warm alcohol; it crystallises in long, fine, silky needles, which felt very easily; its melting-point is 56.5° . Diborneolic formal is a solid white body smelling somewhat of borneol; it is very soluble in ether and benzene, and crystallises in alcohol in pearly flakes; it is fusible at 166° , and distils without decomposition at $344\text{--}345^\circ$.—*Bull. Soc. Chim.*, Series 3, xxi., No. 8.

NOTICES OF BOOKS.

Examination of Water for Sanitary and Technic Purposes. By HENRY LEFFMANN, M.D., Ph.D. Fourth Edition, Revised and Enlarged, with Illustrations. Philadelphia: P. Blakiston's Son and Co. 1899. Pp. 145.

ONLY a few changes have been made in this edition, these being principally improvements in detail. The principal advance in water examination since the last edition has been in bacteriological methods. It is freely admitted that the detection of pathogenic microbes in water is so difficult as to be rarely accomplished; it is therefore, we think, greatly to be desired that in any report condemning a water on pathogenic grounds, details of the method of examination and identification of the microbes should be given in full, so that there may be no question as to the accuracy of the report.

We cannot accept Dr. Leffmann's statement that "it is now generally admitted that mere microbe-counting is of little use in judging of the sanitary value of water-samples" without a slight demur: the actual number of microbes found does not of course imply much, but a competent man who is accustomed to handle numbers of samples can form a very good opinion of the character of the water-samples by the variation in the numbers of the colonies present.

The author deals with the whole range of water analysis, the section on interpretation of results being of special interest and value.

Laboratory Manual. Experiments to Illustrate the Elementary Principles of Chemistry. By H. W. HILLYER, Ph.D. New York: The Macmillan Company. 1899. Pp. 200.

IN Part I. of this volume the preparation and properties of the commoner elements and their compounds are described, together with experiments illustrating the fundamental ideas of Chemistry; and Part II. deals with the verification of the Quantitative Laws. As a text-book it will no doubt fulfil its object; it has, however, one feature to which we must take exception—only one side of each sheet is printed on, the other being left blank; we can see no advantage in this course, and, considering that all these blank pages are numbered, the book appears to have double the number of pages—viz., 200—that it in reality possesses, viz., 100.

Lexicon of the Carbon Compounds. (Lexikon der Kohlenstoff-Verbindungen). By M. RICHTER. In 35 Parts. Hamburg and Leipzig: Leopold Voss. 1899. Parts 1 to 12, pp. 784.

WE cannot but admire the steady and untiring perseverance shown by the author in plodding through the stupendous task he has undertaken—a task apparently hopeless on account of the continuous and ever-increasing additions which are constantly being made to our knowledge of the carbon compounds.

The work of tabulating the carbon compounds was originally commenced in the year 1883, under the title of "Tables of the Carbon Compounds," the compilation of the present "Lexicon" being undertaken in the year 1889, but much delay was occasioned by the work of the Geneva Commission concerning the nomenclature of the aliphatic hydrocarbons in 1892, while the number of registered compounds has increased during the progress of the work from 16,000 to about 65,000 carbon compounds at the present day.

The arrangement of the material and the manner of registering it remains the same as in the original "Tables of Carbon Compounds," but the Tables of Percentages have been extended to the forms CHO, CHN, and CHON, altogether to about 20,000 formulæ.

When complete these volumes will be of immense value to workers in organic chemistry as a book of reference, and too much praise cannot be given to the author for his long and patient labour in compiling such a work,

The Foundations of General Chemistry. (Grundriss der Allgemeinen Chemie). By W. OSTWALD. Third Edition, Enlarged, with 57 Illustrations. Leipzig: Wilhelm Engelmann. 1899. Pp. 549.

As its title indicates, the general tone of this volume is entirely theoretical, and the subject certainly is treated in a masterly manner.

The book is divided into two principal parts, and eleven books, each consisting of four or more chapters. The first part deals with stoichiometry, and the second with relationships between the properties of elements, such as chemical energy, thermochemistry, electrochemistry, photochemistry, &c. There are two comprehensive indices, one of names and the other of subjects.

The book is well arranged, and will prove invaluable to both students and more advanced chemists.

Chemical Industry. (La Chimica Industriale).

WE have received the first two numbers of this new Italian Journal, published in Torino, which is the official publication of the Italian Society of Chemical Industry. The subject matter consists of articles, abstractions, notes, trade notices, &c., filling sixteen pages; it is well printed, and on much better paper than is usually found in continental journals. We wish our new contemporary every success.

The Chemical Trade Directory. Manchester: Davis Brothers. 1899. Pp. 374.

THE compilers of this Directory have aimed at producing a volume which will be of interest and practical use to chemical manufacturers, merchants, agents, brokers, assayers and analysts, &c., in Great Britain and Ireland.

The first three sections—comprising chemical manufacturers, chemical merchants, and makers of plant and material—are compiled from information obtained directly from the firms and individuals concerned. The list of analysts and public samplers will doubtless prove to be of much use, as it often occurs that in cases of dispute the parties to the dispute are unaware of the existence of an analyst or sampler in their neighbourhood, and valuable time may therefore be lost. We congratulate Messrs. Davis Bros. on the production of a very useful volume.

CHEMICAL NOTICES FROM FOREIGN SOURCES

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 16, October 6, 1899.

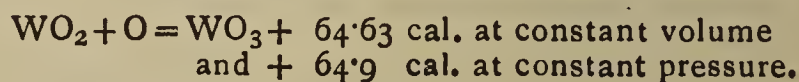
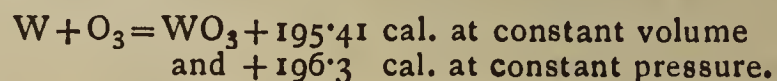
Production of Ozone during the Decomposition of Water by means of Fluorine.—Henri Moissan.—The action of fluorine on water affords a new proof of the easy polymerisation of oxygen to form ozone at a low temperature. The experiments which the author performed in 1891 are now repeated with a larger volume of fluorine, prepared in a copper apparatus. The current of fluorine is led into the water through a small platinum tube—the water being kept at 0°. Attached to the vessel is a bulb into which the liberated gas passes. When the

bulb is full by displacement of the ozonised oxygen, the contents are estimated by means of a solution of potassium iodide in presence of excess of sulphuric acid. The iodine liberated by the ozone is titrated with sodium thiosulphate solution. As much as 143.9 c.c. of ozone was found per litre.

Atomic Weight of Boron.—Henri Gautier.—Of all the non-metallic elements, boron is the one whose atomic weight is the least certain. Since the preparation of pure amorphous boron by M. Moissan, the author has re-determined the atomic weight by employing two compounds of small molecular weight, boron sulphide and boron carbide; both these substances being prepared from pure amorphous boron. The mean of four determinations gives the atomic weight as 11.041, with a probable error of 0.017.

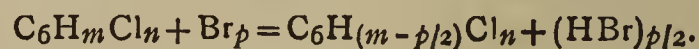
Anhydrous Magnesium Carbonate.—R. Engel.—During a former research on the carbonates of magnesium, the author observed that, when heating the double sesquicarbonate of magnesium and potassium under favourable conditions, there results a mixture of normal potassium carbonate and anhydrous magnesium carbonate. This latter compound differs in many respects from the natural carbonate, especially in its solubility in water and the ease with which it combines with water. It is best prepared by heating the double carbonate of magnesium and ammonium.

Heat of Oxidation of Tungsten.—MM. Delépine and Hallopeau.—The authors have measured the heats of combustion of tungsten and of the suboxide WO₂, in order to compare these numbers with those obtained for other metals, and so to assign a place to tungsten in the series of elements. The numerical results are shown by the following equations:—



Action of Potassammonium on Arsenic.—C. Hugot.—The author, continuing his research, considers two further cases:—(1) When the ammonium alkali is in excess, a yellow amorphous body is formed, slightly soluble in liquid ammonia gas, to which it imparts a yellow colouration. Under pressure and at ordinary temperatures it becomes brick red, analysis showing it to have the formula AsK₃.NH₃. (2) When the arsenic is in excess, a red liquid is formed, which, after being filtered through glass-wool and evaporated, leaves an orange-coloured mass. This compound appears to have the formula As₄K₂.NH₃. When heated to a little below 300° it loses its molecule of ammonia gas, and becomes red in colour.

Action of Bromine on some Derived Chlorated Compounds of Benzene in presence of Aluminium Chloride.—A. Mouneyrat and Ch. Pouret.—Very little is known about the chlorobromate compounds of the aromatic carbides. The authors' research was undertaken in order to find out whether there is a general method of preparation of these compounds, i.e., whether the action takes place according to the equation—



Experiment has verified this hypothesis, and the following compounds have been prepared:—

C ₆ Br ₅ Cl..	melting at 299—300°
C ₆ Br ₄ Cl ₍₁₎ Cl ₍₄₎	„ 278—278.5°
C ₆ Br ₃ Cl ₍₁₎ Cl ₍₂₎ Cl ₍₄₎	„ 260—261°
C ₆ Br ₂ Cl ₍₁₎ Cl ₍₂₎ Cl ₍₄₎ Cl ₍₅₎	„ 246—246.5°
C ₆ Br ₄ < $\begin{smallmatrix} CH^{(3)} \\ Cl^{(4)} \end{smallmatrix}$	„ 258—259°

Berichte der Deutschen Chemischen Gesellschaft.

February 13, 1899.

Contribution to the Study of Hydroxylamine.—

S. Tanatar.—Hydroxylamine acts sometimes as an oxidising and sometimes as a reducing agent. If an aqueous solution of hydrochlorate of hydroxylamine is saturated with sulphurous acid gas, acid sulphate of ammonium is obtained almost quantitatively, $\text{H}_2\text{SO}_3 + \text{NH}_2\text{OH} \cdot \text{HCl} = \text{NH}_4 \cdot \text{HSO}_4 + \text{HCl}$. Perchloride of phosphorus reacts slowly in the cold, and rapidly when heated on hydrochlorate of hydroxylamine, giving chloride of ammonium, nitrogen, and oxychloride of phosphorus. Peroxide of hydrogen reacts on a solution of hydrochlorate of hydroxylamine heated to 50° ; it gives off nitrogen and oxygen, while a part of the hydroxylamine is transformed into nitric acid.

Action of Malonate of Ethyl on Oxide of Mesityl.—

D. Vorlaender.—According to the author, the acid melting at 148° obtained by combining oxide of mesityl and malonic ether and saponifying the oily ether formed, is identical with dimethylhydroresorcin,

$(\text{CH}_3)_2 \begin{array}{l} \text{CH}_2 - \text{CO} = \text{CH} \\ \text{CH}_2 - \text{C} - \text{OH} \end{array}$, which has already been described.

On 1.9-Dimethyluric Acid and 1.7.9-Trimethyluric Acid.—E. Fischer and F. Ach.—There were five dimethyluric and three trimethyluric acids already known; according to theory, there should be six of the former and four of the latter. The authors have succeeded in preparing the other two. The 1.7.9-trimethyluric acid was prepared by treating a warm solution of methyl-9-amino-6-oxy-8-chloro-2-purine with nitrite of sodium. The crystalline powder obtained corresponds to the formula $\text{C}_6\text{H}_5\text{N}_4\text{O}_2\text{Cl} \cdot 0.5\text{H}_2\text{O}$, soluble in boiling alkalis, forming salts; slightly soluble in water, alcohol, and acetic acid. This compound melts at about $310-320^\circ$ with decomposition. The dimethyl 1.9-uric acid is obtained by condensing the corresponding methyl-9-dioxychloropurine with formaldehyde in the presence of dilute potash; it is precipitated in the form of a slightly soluble potassium salt. By treating this salt with iodide of methyl at 80° , dimethyl-1.9-dioxy-6 δ -chloro-2-purine is obtained, and this body, when heated for four hours to 100° in a closed vessel with concentrated hydrochloric acid, gives dimethyl-1.9-uric acid, crystallising in rectangular tables melting with decomposition at about 400° .

Observations on the Purine Group.—E. Fischer.—This paper consists of a number of separate observations which contribute to our knowledge of the constitution of the purines. When an alcoholic solution of methyl-9-trichloropurine, saturated with ammonia gas is heated to 100° a mixture of methyl 9-dichloradenine and methyl-9-amino-8-dichloro-2.6-purine is obtained. Dimethyl-3.9-uric acid, heated with perchloride and oxychloride of phosphorus to $145-155^\circ$ for six or seven hours gives methyl-9-oxy-8-dichloro-2.6-purine, fusible at $272-273^\circ$. Oxychloride of phosphorus reacts at about 140° in a closed vessel on methyl-7 uric acid, giving methyl-7-oxy-8-dichloro-2.6-purine. This latter, in its turn, furnishes methyl-7-trichloropurine when heated to $155-160^\circ$ for five hours with a mixture of perchloride and oxychloride of phosphorus.

Action of Hydrochloric and Hydrobromic Acids on the Aromatic Nitroso-derivatives.—E. Bamberger, H. Busdorf, and B. Szolayski.—Hydrochloric acid transforms nitrosobenzene first into phenylchlorhydroxylamine, $\text{C}_6\text{H}_5\text{N} \begin{array}{l} \text{OH} \\ \text{Cl} \end{array}$; this body becomes rapidly isomerised, giving *p*-chlorophenylhydroxylamine, $\text{Cl} \cdot \text{C}_6\text{H}_4 \cdot \text{NHOH}$. The action of hydrobromic acid on nitrosobenzene is entirely analogous. The results are also analogous with *p*-nitrosotoluene, but cresols are obtained in addition.

Products of Condensation of Formic Aldehyde with Quinaldine.—W. Koenigs.—Quinaldine will unite

with 1, 2, or 3 molecules of formic aldehyde. The 3 atoms of hydrogen of the methyl group united with the nitrogen are replaced successively with 1, 2, or 3 CH_2OH -groups, forming α -quinolyethanol, $\text{C}_9\text{H}_6\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2\text{OH}$; α -quinolylpropanediol, $\text{C}_9\text{H}_6\text{N} \cdot \text{CH}(\text{CH}_2\text{OH})_2$; and α -quinolylbutanetriol, $\text{C}_9\text{H}_6\text{N} \cdot \text{C}(\text{CH}_2\text{OH})_3$.

Bulletin des Travaux de la Société de Pharmacie de Bordeaux, May, 1899.

This issue contains no chemical matter.

June, 1899.

On a Coloured Reaction of Alcaptone.—G. Denigès.—In the presence of persulphate of ammonium or the peroxides of lead and manganese in alkaline solution, alcaptone (homogentisic acid) gives a very marked reddish brown colouration, even when present in very small quantity. For its detection in urine, 0.5 to 1 grm. of oxide of lead is placed in a test-tube with 10 c.c. of the urine, and three or four drops of potash or soda-lye; this should be well shaken up for a few minutes and filtered. If the urine is normal its colour remains unchanged, but if alcaptone is present it becomes distinctly red. If peroxide of manganese is used instead of peroxide of lead, the colour will be more inclined to brown.

On Effervescing Water, so-called "Seltzer."—P. Carles.—The author points out that very often insufficient care is exercised from the hygienic point of view in the manufacture of so-called "mineral waters," such as seltzer, &c. The three principal things to take note of are:—(1) The judicious choice of a soft water; (2) to use only perfectly pure carbonic acid; and (3) not to allow the use of valves made partially of lead. He points out that it has been shown by Duclaux that, in times of epidemics, chance is the principal factor which governs the bacteriological purity of the water, and that the microbes of typhoid, for example, will live for a longer time in seltzer water than in ordinary tap-water or distilled water.

July, 1899.

Glycerophosphate of Lime.—P. Carles.—It is generally admitted that, of the glycerophosphates, that of lime is the one to be preferred. This, however, is not very soluble; its coefficient of solubility being from 3.3 to 6 per cent according to different authors. The author has endeavoured to account for this rather wide variation. He found that the maximum of solubility of the crystallised neutral glycerophosphate of lime was reached at 28° ; if the temperature be increased above this point, the solubility rapidly decreases, and it becomes almost insoluble again. He confirms the results of other writers, that the addition of a little acid greatly increases the solubility of the salt, but he does not recommend the use of citric acid, as an insoluble citrate of lime is gradually formed; oxalic acid gives much better results. One hundred grms. of the neutral powdered glycerophosphate should be added to 800 grms. of warm water; 30 grms. of oxalic acid is then dissolved in 100 grms. of boiling distilled water. These two solutions must be thoroughly mixed and filtered; the precipitate is washed until the filtrate is one litre in volume. The solution is perfectly clear, and contains no trace of oxalic acid, and is also very stable, even after prolonged heating on the water-bath.

Volumetric Estimation of Aniline by Bromine and Bromine by Aniline.—G. Denigès.—Already noticed in this column.

The presence of Estragol in Essence of Chervil.—E. Charabot and L. Pillet.—The authors have examined a quantity of freshly sown chervil (*Chærophyllum sativum*), from which they obtained 4.25 grms. of essence in the form of a pale yellow oil. The result of their experiments with, and analysis of, this oil shows that estragol is the principal constituent of essence of chervil.—*Bull. Soc. Chim.*, Series 3, xxi., No. 8.

MISCELLANEOUS

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 6th instant, His Grace the Duke of Northumberland, K.G., President, presiding. The following were elected members:—H.H. The Thakore Saheb of Gondal, G. F. Barrett, J. B. Broun-Morison, A. H. Savage Landor, and T. C. Porter. The special thanks of the Members were returned to "A Lady Member" for her donation of £100, and to Mr. George Matthey, F.R.S., for his donation of £100 to the fund for the Promotion of Experimental Research at Low Temperatures. The special thanks of the Members were returned to Miss Elinor Busk and Miss Frances Busk for a portrait of Mr. George Busk, F.R.S., Treasurer of the Royal Institution from 1873 to 1886.

Merck's "Digest," Nos. 4 and 5.—These two numbers deal respectively with tannoform and largin. The former is a condensation product of tannin and formic aldehyde, having the formula $C_{29}H_{20}O_{18}$. It occurs as a loose reddish-white powder, insoluble in water, but soluble in alcohol, ammonia water, and solution of soda or sodium carbonate; it melts with decomposition at 230°. It is recommended as a perfectly safe and innocuous antihidrotic and antiseptic siccative; compared with salicylic acid it is said to be more pleasant and more efficacious. Largin is an albumen and silver compound, the albumenoid component of which is protalbin, a new derivative of the para-nucleo-proteids. The preparation is a whitish-grey powder, soluble in alcohol, 10.5 per cent of which is taken up by water at the ordinary temperature; it possesses powerful bactericidal properties, and will easily penetrate tissues.

MEETINGS FOR THE WEEK.

WEDNESDAY, 15th.—Society of Arts, 8. Opening Address of the 146th Session, by Sir John Wolfe Barry, K.C.B., V.P.Inst.C.E., F.R.S.

THURSDAY, 16th.—Chemical, 8. "The Chlorine Derivatives of Pyridine—Part IV., Constitution of the Tetrachloropyridines," by W. J. Sell, M.A., and F. W. Dootson, M.A. "Contributions to our Knowledge of the Aconite Alkaloids—Part XV., On Japaconite, and the Alkaloids of Japanese Aconite," by W. R. Dunstan, F.R.S., and H. M. Read, "On the Determination of Transition Temperatures," by H. M. Dawson, Ph.D., and P. Williams, B.Sc.

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MICHAELMAS TERM.—Monday, October 2, to Saturday, December 16.

LENT TERM.—Monday, January 8, to Saturday, April 7.

EASTER TERM.—Monday, April 30, to Saturday, July 28.

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THE CHEMICAL NEWS

VOL. LXXX, No. 2086.

A BIBLIOGRAPHY OF STEEL-WORKS ANALYSIS.

By HARRY BREARLEY.

WITH the intention of realising what changes had taken place in steel analysis since analytical chemistry became adapted to steel-making, I began with volume I. of the CHEMICAL NEWS, and, without pretending to read—much less study—scanned its pages, noted the volume, page, and author of the articles I was likely to be interested in, and read a particularly interesting paper here and there. These references, put in order, have been of great service whenever difficulties or doubts have cropped up. Many helpful details were at once made use of. Many series of lectures and investigations by Faraday, Tyndall, Odling, Frankland, Miller, Crookes, Percy, Calvert, Letheby, Angus-Smith, Forbes, and a number of others, are comprehensive demonstrations of every-day phenomena, of physical and chemical laws, or models of prolonged and delicate investigations. To the hundreds of half-educated analysts who, like myself, were not prepared for the work, but eagerly accepted it as the best available means of earning a living, a better and more practicable way could hardly be recommended of shaking off blarney eyes and narrowness, and of learning patience and perseverance and reverence.

The above form of indexing, together with frequent experiment, has led to a bibliography of a partial kind, which, although particularly valuable to myself, may be of considerable value to others also. It refers to every element usually estimated in the materials generally examined in a steel works laboratory.

The compilation, with few exceptions, is made from the following readily accessible journals:—

- The CHEMICAL NEWS, 1860 to 1899, vols. i. to lxxix.
- The Journal of the Chemical Society, 1885—1898, vols. xlvii. to lxxiv.
- The Journal of the Iron and Steel Institute, 1880 to 1899.

Owing to the numerous reprints and abstracts these journals contain, the area covered is a very large one. The source of the reprint or abstract is not given here. I am sorry to have had no opportunity of examining other English journals, particularly the *Journ. Soc. Chem. Industry*, but hope to do so for some of the rarer elements whose modes of estimation are neither so numerous nor so well established as is that of carbon or manganese.

Fresenius's "Quantitative Chemical Analysis" abounds in references, but they are mainly to foreign journals not easily accessible, and, providing they were, there are enough analysts unable to read either German or French to make a supplementary reference to an English reprint, or even abstract of the paper referred to, of considerable value in an English translation of that admirable treatise.

The following synopses illustrate lamentable differences in the working of the same process. If every steel works laboratory could be stimulated to observation with experiment, there would soon be fewer such disagreeable discrepancies and direct contradictions. Lord Rayleigh's philosophy, if taken to heart, would do a great deal in this direction. "One's instinct at first is to try to get rid of a disagreeable discrepancy; but I believe that experience shows such an endeavour to be a mistake. What we ought to do is to magnify a discrepancy with a view of finding out the explanation" (C. N., lxxi., 300).

There is a little indefiniteness about the classification

of the means of estimating an element. Some marked feature, such as the final state, has had to be fixed on, although the most diverse processes may lead up to it.

A number of papers have been neglected, on the ground that they contain only commonplace information or points which are already well covered by the papers noticed. Such bibliographical errors are inseparable from a synopsis made to assist one in every-day operations and chiefly for personal use.

If an English reprint of a paper is available, that is referred to. Where there is an abstract only, reference is commonly made to one journal only. In many cases a similar abstract may be found in the corresponding volume of the other journals.

MANGANESE.

THE following classification is adopted:—

- I. SEPARATING THE IRON.
 - a. Precipitating the Iron.
 1. As Acetate. 2. Sulphate. 3. Phosphate.
 4. Hydrate. 5. Other Reagents.
 - b. Precipitating the Manganese.
- II. SEPARATING OTHER ELEMENTS.
- III. GRAVIMETRIC ESTIMATION OF MANGANESE.
 - a. As Mangano-manganic Oxide.
 - b. As Manganese Pyrophosphate.
 - c. As Manganese Sulphate.
 - d. As Manganese Sulphide.
 - e. As Manganese Carbonate.
 - f. Electrolytically.
 - g. Miscellaneous.
- IV. VOLUMETRIC ESTIMATION OF MANGANESE.
 - a. Titrations with Standard Permanganate.
 - b. Oxidations to Permanganate.
 - c. Oxidations to Higher Oxides of Manganese.
 1. The Chlorate Process.
 2. Other Oxidimetric Processes.
 3. Available Oxygen in Ores, &c.
 - d. Indirect Processes.
 - e. Miscellaneous Processes.
- V. DETECTION OF MANGANESE.
- VI. MISCELLANEOUS NOTES.

I. SEPARATION OF IRON.

- a.1. *Precipitating the Iron with Acetate (Succinate or Formate).—*
1. KESSLER (C. N., xxvii., 14).—Explains the state of a solution of ferric chloride when soda carbonate is added to faint precipitation. Imperfect separations are due to excess of acetate; a minimum quantity stated.
2. ROSENTHAL (C. N., xxxvi., 147).—A re-precipitation by the acetate process is quite unnecessary.
3. JEWETT (C. N., lx., 273).—Five per cent free acetic acid causes complete separation when large amounts of soda acetate are used. The same is true for zinc and nearly so for Ni and Co.
4. MEINECKE (Z. C. S., lvi., 309).—The successful separation depends on perfect neutralisation, small amounts of acetate and acetic acid, and short rapid boiling.
5. BREARLEY (C. N., lxxv., 13).—Free acetic acid corrects errors due to large excesses of acetate. Separations complete with one precipitation without free acetic if small amount of acetate is used.
6. RIGGS (Z. C. S., lxii., 536).—There is danger of a little Mn separating as higher oxide when the solution is neutralised previous to acetate separation.
7. TAMM (C. N., xxvi., 37).—Precipitates with succinates. Objects to oxidation of iron with HNO₃, because part of the Mn is then always in Mn₂O₃ state and precipitated with the Fe; recommends KClO₃, or evaporation of HNO₃ entirely.

8. FRESSENIUS ("Quant. Anal."). — Basic formates are more easily washed than acetates. Succinates are said to completely precipitate Al along with the Fe. (Basic acetate separations will be more fully treated under "Nickel").

I.a. 2. *Precipitating the Iron with Sulphates.*—

9. KESSLER (*J. I. S. I.*, 1880, 353).—Mixed chlorides are thoroughly neutralised with Na_2CO_3 ; the diluted solution is precipitated in the cold with Na_2SO_4 , and straightway filtered. (A translation of this paper appears in *Iron*, May 31, 1879).
10. MEINECKE (*J. C. S.*, lvi., 310).—Precipitates with $(\text{NH}_4)_2\text{SO}_4$ at ordinary temperatures. Mn, Ni, Co, Cu, and Zn are in solution, and Al partly.
11. RUPP (*J. I. S. I.*, 1896, i., 535).—Solution neutral, but no definite precipitate; 18 c.c. 10 per cent Na_2SO_4 precipitates 4 gms. Fe in the cold; filtrate titrated with permanganate.

I.a. 3. *Precipitating the Iron with Phosphates.*—

12. BLOXAM (*C. N.*, l., 112).—Speaks unfavourably of the acetate process.* Precipitates neutralised iron solution with ammonium acetate and excess of soda phosphate; ferric phosphate re-dissolved and re-precipitated; Mn in filtrate estimated as $\text{Mn}_2\text{P}_2\text{O}_7$.

I.a. 4. *Precipitating the Iron as Hydrate.*—

13. SARNSTROM (*C. N.*, xlvii., 177).—Preparatory to estimating the Mn by Guyard's process, the Fe is precipitated by a small excess of soda bicarbonate. (See 95, 96, and 97).
14. MEINECKE (*J. I. S. I.*, 1888, ii., 326).—Fe solution saturated with CO_2 , neutralised with soda bicarbonate, and carefully coagulated with a drop more. Precipitate free from Mn, Co, and Ni. Process not available in presence of much Al. Phosphate method of precipitating Fe worthless; precipitation with HgO of little use; BaCO_3 always leaves Mn in precipitate. See also *J. C. S.*, lvi., 310, for separation of other elements by a similar process.
15. FRESSENIUS ("Quant. Anal.," p. 437, 7th ed.).—Add ammonium carbonate so that fluid loses its transparency and tends to become more turbid rather than otherwise, then boil; the iron is precipitated. Described also by Dittmar ("Quant. Anal.," p. 74). Known as Schwarzenberg or Herschell's method.

I.a. 5. *Iron Precipitated by various Reagents.*—

16. Zinc Oxide.—VOLHARD (*C. N.*, xl., 207; *J. I. S. I.*, 1880, 355).—Dilute H_2SO_4 solution of the metals neutralised with soda carbonate; emulsion ZnO added until complete precipitation of Fe is indicated by sudden coagulation of the solution.
17. Ammonium Chloride.—KERN (*C. N.*, xxxiii., 90).— $\text{Fe}_2\text{Cl}_6 + \text{MnCl}_2$ precipitated with KHO , large amount $(\text{NH}_4)\text{Cl}$ added and boiled; the filtrate contains the Mn. It is further precipitated as sulphide and estimated as sulphate.
- KERN (*C. N.*, xxxv., 270).—Powdered sample mixed with $(\text{NH}_4)\text{Cl}$ and strongly ignited; process repeated until Fe is volatilised. Residue separated from SiO_2 , &c., is weighed as Mn_3O_4 (see 58).
18. Barium Carbonate.—FORBES (*C. N.*, xvi., 105), and JUPTNER (*J. I. S. I.*, 1885, i., 247), separate Fe with BaCO_3 (see 14).
19. Chlorine.—KERN (*C. N.*, xxxv., 247).—Precipitate Fe and Mn together with ammonia. Volatilise Fe in current of Cl; estimate residue as Mn_3O_4 .
- 19a. FRIEDMANN (*J. I. S. I.*, 1888, ii., 328).—Volatilise Fe in Cl. Graphite, Cu, Co, Ni, Mn, and slag in the residue.

20. Sulphuretted Hydrogen.—CARNOT (*J. I. S. I.*, 1887, i., 470).—Acetate added to neutralised solution and H_2S passed through; Fe, Ni, and Co are completely precipitated.

21. Lead Carbonate.—CAMPBELL (*J. C. S.*, lxii., ii., 103).—Ferric solutions are precipitated by PbCO_3 . Mn, Co, Ni and ferrous salts are not decomposed. Warming assists the reaction; nitrate should be absent.

22. Lead Oxide.—FIELD (*C. N.*, i., 4).—Mn, Ni, and Co are separated from Fe by precipitating with this reagent.

23. Soda Nitrite.—WYNKOOP (*J. C. S.*, lxxiv., ii., 54).—Fe, Cr, Al are completely separated from Mn, Zn, Ni, Co, by boiling with excess of NaNO_2 . It is best to have Fe in the ferrous state.

24. Ether.—SKEY (*C. N.*, xvi., 201) suggests a separation by abstracting the Fe with ether from a solution of the sulphocyanides.

25. Nitroso- β -naphthol. — KNORRE (*C. N.*, lix., 232; *J. I. S. I.*, 1887, i., 470).—Fe must be present as sulphate or chloride; neutralised solution precipitated with at least ten times as much of the reagent, dissolved in acetic acid, as there is Fe present. By the same process Fe is separated from Cr, Ni, Zn, and Al. See also De Koninck, *CHEM. NEWS*, lxii., 19

26. BURGASS (*J. C. S.*, lxxii., ii., 162).—Nitroso- β -naphthol precipitates, Cu, Co, and Fe completely; Mn, Hg, Ni, Cr, Pb, Zn, Al, Cd, Mg, Ca, Bi, Sb, and As remain in solution.

27. Electrolytic.—KOEPEL (*J. C. S.*, lxxiv., ii., 354).—Solution of Fe and Mn sulphates are poured into boiling soda pyrophosphate. The Fe is deposited from the clear solution.

I.b. *Precipitating the Manganese.*—

28. BEILSTEIN and JAWAIN (*C. N.*, xl., 300; *J. I. S. I.*, 1880, 354).—Solution of the metals poured into concentrated KCN; the Mn is precipitated with iodine and converted into sulphide. Describes also the chlorate process, which is really a separation in which the manganese is precipitated.

29. MOORE (*C. N.*, lvii., 125).—Sodium carbonate in excess added to concentrated solution of the metals; dissolve precipitate in KCN, add a little KHO , and precipitate Mn with H_2O_2 . The Mn may also be precipitated with H_2S . Ni and Co are also precipitated.

30. CLASSEN (*C. N.*, xl., 33).—Manganous solutions are precipitated by neutral potassium oxalate; the precipitate being soluble in excess. The potassium manganous oxalate is decomposed by concentrated acetic acid, but the potassium ferric oxalate remains dissolved. Zn or Mg chlorides, used to obviate influence of alkaline chlorides. The process separates Ca, Co, Ni, and Cu from Fe and Al, and is later elaborated (*C. N.*, xl., 196) to cover a number of other separations.

31. BLUM (*C. N.*, lv., 236).—HCl solution of chlorides mixed with tartaric acid, so that no precipitate is formed with ammonia; ferricyanide added. Mn, Ni, Co, and Zn are precipitated. Filters badly.

32. ENGELS (*J. C. S.*, lxxiv., ii., 192).— MnO_2 is precipitated by the electric current from an acidulated solution of the sulphates.

(To be continued).

Christmas Lectures at the Royal Institution.—The Annual Course of Christmas Lectures, specially adapted for young people, at the Royal Institution, will this year be delivered by Mr. Charles Vernon Boys, F.R.S. The subject will be "Fluids in Motion and at Rest." The Lectures (which will be six in number) will commence on Thursday, December 28, at Three o'clock. The remaining Lectures will be delivered on December 30, and on January 2, 4, 6, and 9, 1900.

* "The advocate of one method often makes the other suffer by comparison, more by reason of his own want of skill in the manipulation of the other method than by reason of any great advantage in his own" (Blair, *C. N.*, lvi., 246).

METHOD FOR THE ESTIMATION OF SILICON IN FERRO-CHROMIUM, AND OF SILICA IN CHROME ORE.

By GEORGE TATE, Ph.D., F.I.C.

ONE to two grms. of ferro-chromium or of ore are fused with about five times their weight of sodium peroxide in a nickel crucible. The crucible and contents, after cooling, are brought into water contained in a capacious nickel dish. The alkaline liquid so obtained containing chromate and silicate, together with oxides of iron and nickel in suspension, is treated with hydrochloric acid in quantity insufficient to neutralise the alkali, and then evaporated to dryness in the nickel dish. The residue is scraped, as far as is practicable, from the sides to the bottom of the dish, and 40 c.c. of strong pure sulphuric acid rapidly poured on. Fumes of hydrochloric and chlorochromic acids are evolved, and completely expelled by applying heat. The temperature is raised until the sulphuric acid begins to fume, thereby ensuring the dehydration of silicic acid. After removal of the flame and cooling for a few minutes, water is cautiously added. To prevent undue corrosion of the nickel vessel, the turbid liquid is transferred to a porcelain dish, and, after making the bulk about $\frac{1}{4}$ litre, boiled for fifteen to thirty minutes, or until the sulphates have completely dissolved. The silica is filtered off, washed thoroughly, ignited in a platinum crucible, and weighed. The silica so obtained should be white, but, as a few m.grms. of metallic oxides usually accompany it, the real weight of SiO_2 (from which the silicon is deduced) is obtained by determining the loss in weight occasioned by evaporation with hydrofluoric acid and one drop of sulphuric acid, followed by strong ignition.

It is advisable to test the purity of the reagents by conducting a blank test.

The results are very concordant and apparently exact. Experiments have shown that 90 to 95 per cent of the chromium can be volatilised by the action of the sulphuric acid; the removal of the chromium prevents the contamination of the silica by basic salts of that metal.

Test experiments, wherein known weights of silica were fused with bichromate and sodium peroxide, and the products submitted to the above treatment, have shown that the process brings practically the whole of the silicon into a weighable form.

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EVOLUTION OF CHEMISTRY IN THE LAST TWENTY YEARS.*

By Dr. A. LADENBURG.

(Concluded from p. 227).

SINCE the observations of Ste. Claire-Deville, the phenomena of dissociation has been regarded and treated as analogous to those of evaporation. Van't Hoff now shows that there are reactions which are comparable with the process of fusion, and in which a fixed temperature marks the line of separation between two chemically different conditions. This fixed temperature he designates the transition temperature; and he demonstrates the accuracy of his idea in the cases of the formation of double salts (astrakanite), of the preparation of elements in allotropic modifications (sulphur), and of the splitting of racemic substances (sodium ammonium racemate).

He afterwards treated this subject in a much more detailed manner in an important monograph, "On the Formation and Splitting of Double Salts," in which he

explains the theory of the matter, and describes the methods for experimentally determining the transition temperature.

These investigations have found very important applications in relation to the deposition of salts from ocean water, and in explaining the splitting of racemic compounds by Pasteur's methods.

This leads us directly to the subject of stereo-chemistry, which has already been discussed, but which has acquired so much importance of late that I must return to it here.

After the propounding of the theory by van't Hoff and Le Bel, it was only isolated investigations that were, in the first place, carried out with a view to testing it—such, for example, as the splitting by means of fungi of a series of alcohols, which Le Bel succeeded in doing; and the splitting of synthetic coniine, which was of importance inasmuch as it was the preparation, for the first time, of an active base. The theory was subjected to a systematic examination by Emil Fischer, in carrying out his well-known syntheses in the sugar group.

It is simply astonishing that the theory stood the test of this *experimentum crucis*, and that the sagacity of Fischer enabled him to fix the configurations of the individual hexoses without encountering any contradictions in doing so, especially when we take into consideration the recent experiments of Walden, in accordance with which it is possible, by means of simple chemical reactions, to pass at ordinary temperatures from an active substance to its enantiomorph.

As regards the application of the theory of asymmetric carbon atoms to molecules with doubly linked carbon atoms—a matter that van't Hoff had already mentioned, but one which had met with less attention—very special notice was called to it by Wislicenus, who, moreover, had himself given the first impulse to stereo-chemical conceptions by his earlier and extended investigations of lactic acid.

The researches of Wislicenus and his pupils have certainly supplied most valuable contributions towards the clearing up of these remarkable cases of isomerism—an end towards which (after the discovery of fumaric and maleic acids) a great many chemists, and even Kekulé himself, had aspired in vain. In this domain, however, there are still many unexplained contradictions, as Michael and Auschütz in particular have shown. On the other hand it must be admitted, that by van't Hoff's theory an extremely plausible explanation of the products arising from the oxidation of fumaric and of maleic acids is rendered possible.

The applications of the doctrine of asymmetric carbon atoms to substances containing rings are also important and interesting. The first principles were laid down by van't Hoff; but their significance was only fully recognised when Baeyer published his extended investigations upon hydrogenised aromatic compounds, and, in particular, upon the hydrophthalic acids.

While Baeyer's intention in these investigations was to discover weaknesses in the theory, and even to modify it, his labours led instead to a further confirmation of it. Besides this, the credit is due to him of having advanced the so-called tension theory, which has already proved of service in some cases.

Emphasis must be laid upon the fact that the important consequences which the theory of the asymmetric carbon atom brought forth, gave a spur to the more and more complete application of stereo-chemical considerations. In this connection the numerous researches may be mentioned which deal with the non-occurrence of certain reactions, and explain this on stereo-chemical grounds. Amongst these investigations the best known are those of Victor Meyer on the formation of esters. The asymmetry of the nitrogen atom also falls to be mentioned in this connection.

The researches of Hantzsch and Werner were of fundamental significance with respect to the last-named subject, and they were capable of explaining the isomerism amongst

* Read before the British Association (Section B), Dover Meeting, 1899.

oximes, which was already familiar at that time. Hantzsch afterwards extended the views respecting this matter, and turned them to account in explaining the isomeric hydrazones and diazo-compounds. It is true that it was only geometrical isomerism in the case of nitrogenous organic compounds that was proved by these investigations. Le Bel and Ladenburg endeavoured to prove that asymmetric nitrogen can further produce or influence optical activity. The investigations of both have, however, been attacked, but Ladenburg has been able to establish the accuracy of his results.

Another subject that was much discussed was the significance of racemism, about which a clear understanding only became possible upon the introduction of the conception of the transition temperature, and upon the recognition of the analogy between racemic substances and double salts. The most important method of splitting racemic substances—that by means of optically active substances—remained a standing enigma as long as the existence of partially racemic substances was denied. Every difficulty was removed, however, after Ladenburg had shown that such substances do without doubt exist, and after a transition temperature had been recognised in their case also.

Furthermore, the much debated question as to how a truly racemic substance (inactive by intra-molecular compensation) can be distinguished from the mixture of the active components, may now be looked upon as practically settled.

It is beyond doubt that the founding and development of stereo-chemistry (a name which originated with Victor Meyer) is the most important thing that has been accomplished in organic chemistry during the last two decades. Stereo-chemistry possesses a significance for this period similar to that which the foundation and introduction of the theory of aromatic compounds possessed for the twenty years preceding. There are besides, however, other important investigations in organic chemistry which require to be mentioned.

The systematic and, theoretically, almost completed examination of the sugar group has already been referred to. The uric acid group, which so long resisted elucidation and synthesis, is now completely cleared up, and this is chiefly due to Emil Fischer's synthetical investigations.

The hydrogenised aromatic compounds have likewise been referred to already, but the terpenes have not been mentioned. The latter formerly constituted one of the most confused sections of organic chemistry, whereas Wallach has now succeeded in systematising them by his extended and careful researches. But the most important thing about them, the elucidation of their constitution, is still wanting; for, in spite of some fortunate dashes by Baeyer, which led to the synthesis of substances resembling terpenes, no one has yet succeeded in clearing this up.

The discovery of the iodo-, iodoso-, and iodonium-compounds, for which we are indebted to Willgerodt and to Victor Meyer, is also important, and these compounds supply new knowledge concerning the nature of iodine. The discovery of antipyrine by Knorr was of great importance in medicine, and through it the pyrazol group came to be simultaneously explored.

The preparation of the so-called substantive azo-dyes has become of technical importance; and that of synthetic indigo, according to a method discovered by Heumann, promises to become so.

Great advances have likewise been made in the preparation of artificial perfumes. Vanilline has already been referred to. The manufacture of piperonal (heliotropine), and especially the synthesis of ionone by Tiemann and Krüger, fall to be mentioned in this connection.

This account of the most recent phases in the development of our science must not be concluded, however, without reference being made to the valuable, although unfinished, researches which were carried out under the direction of Friedel, and which aimed at the introduction of a new nomenclature into organic chemistry. Even al-

though it has not yet been possible to extend the system to substances containing rings, still there is much that is good and valuable in the principles that have been advanced.

PHOTO-CRYSTALLISATION.*

By FERDINAND G. WIECHMANN, Ph.D.

(Concluded from p. 227).

Calculation of the Results of Analysis.

LET :—

a = amount of sucrose present.

b = amount of total reducing sugars present.

x = amount of dextrose present.

y = amount of levulose present.

s = the specific rotatory power of sucrose divided by 100.

d = the specific rotatory power of dextrose divided by 100.

l = the specific rotatory power of levulose divided by 100.

p = polarisation observed, expressed in circular degrees.

Then,—

$$(as + xd) - yl = p.$$

$$(as + xd) = p + yl.$$

$$xd = p + yl - as.$$

$$x = \frac{p + yl - as}{d}.$$

Substituting this value of x in the equation—

$$x + y = b,$$

there results—

$$\frac{p + yl - as}{d} + y = b.$$

$$p + yl - as + yd = bd.$$

$$yl + yd = bd - p + as.$$

$$y(l + d) = bd - p + as.$$

$$y = \frac{bd - p + as}{l + d}.$$

As y represents the amount of levulose, y deducted from b will give at once the amount of dextrose. Or, if preferred, the value of x can also easily be calculated independently.

Analytical Results.—The analytical results secured were tabulated and here follow. Table VI. records the analytical data obtained; Table VII. shows the percentage composition of the different specimens as calculated from these data.

TABLE VI.

No. of sample.	Polarisation of a 10 per cent solution at 20° C. in a 200 m.m. tube.	Amount of copper reduced.					
		After inversion.			Before inversion.		
		Duplicate determinations.	Average of duplicate determinations.	Duplicate determinations.	Average of duplicate determinations.	Duplicate determinations.	Average of duplicate determinations.
1.	− 11.7	0.2912	0.2908	0.2910	0.2854	0.2848	0.2851
2.	− 8.2	0.2914	0.2917	0.2915	0.2667	0.2683	0.2675
3.	− 10.8	0.2900	0.2908	0.2904	0.2822	0.2826	0.2824
4.	− 4.8	0.2919	0.2941	0.2930	0.2497	0.2508	0.2502
5.	− 11.4	0.2931	0.2939	0.2935	0.2837	0.2855	0.2846
6.	+ 9.4	0.3001	0.3009	0.3005	0.1863	0.1852	0.1858
7.	− 8.9	0.2765	0.2800	0.2783	0.2721	0.2710	0.2715
8.	− 6.3	0.2960	0.2968	0.2964	0.2717	0.2708	0.2713
9.	− 1.4	0.2808	0.2806	0.2807	0.2691	0.2695	0.2693
10.	− 4.0	0.2929	0.2939	0.2934	0.2490	0.2510	0.2500
11.	− 9.6	0.2840	0.2846	0.2843	0.2778	0.2788	0.2783
12.	+ 9.8	0.3042	0.3032	0.3037	0.1857	0.1866	0.1861
13.	− 4.4	0.2830	0.2855	0.2842	0.2717	0.2741	0.2729
14.	− 6.5	0.2906	0.2934	0.2920	0.2685	0.2683	0.2684
15.	− 5.8	0.2808	0.2797	0.2803	0.2714	0.2708	0.2711
16.	− 0.2	0.3000	0.2998	0.2999	0.2541	0.2539	0.2540
17.	− 2.9	0.2833	0.2849	0.2841	0.2738	0.2723	0.2731
18.	+ 9.0	0.3033	0.3045	0.3039	0.1871	0.1868	0.1869

* School of Mines Quarterly, vol. xvii., No. 4.

TABLE VII.

Number of specimen.	Percentage composition.			Ratio.	
	Sucrose.	Dextrose.	Levulose.	Dextrose.	Levulose.
1.	2.04	46.03	49.11	1	1.06
2.	8.17	43.36	45.52	1	1.05
3.	2.74	46.18	48.04	1	1.04
4.	14.53	40.54	42.19	1	1.04
5.	3.03	45.86	49.16	1	1.07
6.	38.39	32.07	28.31	1	0.88
7.	2.27	46.11	44.18	1	0.96
8.	8.58	46.24	43.99	1	0.95
9.	3.85	53.63	35.87	1	0.67
10.	14.71	41.34	41.33	1	1.00
11.	2.10	46.90	45.79	1	0.98
12.	39.44	32.10	28.34	1	0.88
13.	3.91	50.88	39.84	1	0.78
14.	8.11	45.52	43.60	1	0.96
15.	3.15	49.21	40.90	1	0.83
16.	15.70	46.23	37.86	1	0.82
17.	3.79	52.72	38.06	1	0.72
18.	39.21	31.47	29.28	1	0.93

This table exhibits some interesting relations.

The sucrose originally present has been partly transformed into invert sugar. The increase of invert sugar over and above the amount originally present in the solutions can be gathered from the following:—

TABLE VIII.

Specimen number.	Conditions to which specimens were subjected.		Percentage amount of sucrose inverted.
1.	Sunlight	Acid	7.06
2.	"	Neutral	0.93
3.	"	Acid	16.66
4.	"	Neutral	4.87
5.	"	Acid	38.97
6.	"	Neutral	3.61
7.	Diffuse daylight	Acid	6.83
8.	"	Neutral	0.52
9.	"	Acid	15.55
10.	"	Neutral	4.69
11.	"	Acid	39.90
12.	"	Neutral	2.56
13.	Darkness	Acid	5.19
14.	"	Neutral	0.99
15.	"	Acid	16.25
16.	"	Neutral	3.70
17.	"	Acid	38.21
18.	"	Neutral	2.79

Inversion has proceeded very much more rapidly in the acid solutions than in the others. The amount of sucrose inverted in the corresponding members of each of the three series is fairly constant. Thus in—

Specimen number—	Sucrose inverted.
1	7.06
7	6.83
13	5.19
3	16.66
9	15.55
15	16.25
5	38.97
11	39.90
17	38.21

And again—

Specimen.	Sucrose inverted.
2	0.93
8	0.52
14	0.99

Specimen.	Sucrose inverted.
4	4.87
10	4.69
16	3.70
6	3.61
12	2.56
18	2.79

These results were to be anticipated and are in perfect accord with the teachings of the ion theory; inversion was more rapid in the acid than in the neutral solutions because the inversion of sucrose is proportional to the number of free hydrogen ions present. The total amount of inversion produced is practically the same in the corresponding members of the different series, because the amount of acid used to produce inversion was the same in all instances.

The last two columns of Table VII. show the ratio which obtains between the dextrose and the levulose of the specimens analysed.

Disregarding series, and considering all of the specimens studied, it will be seen that, in those which were wholly solid when analysed, the dextrose-levulose ratio is as follows:—

Specimen number.	Ratio of Dextrose to Levulose.	
1.	1	1.06
2.	1	1.05
3.	1	1.04
4.	1	1.04
5.	1	1.07
7.	1	0.96
10.	1	1.00
11.	1	0.98
14.	1	0.96
Average		1.018

That is to say, the ratio between the dextrose and the levulose in the crystalline solids is practically one to one.

This is confirmatory of the view generally accepted regarding the composition of invert sugar, the molecular mass of which is expressed by the formula $2C_6H_{12}O_6$.

The existence of invert sugar as a definite crystalline solid would thus seem to be clearly established. In recognition of this fact it appears to the writer that it would be entirely appropriate to designate this substance as *invertose*, a name indicative of the origin of this sugar, and at the same time suggestive of its individuality.

The sucrose found associated with invertose in the specimens studied ranges from 2.04 to 14.71 per cent. These crystalline compounds of sucrose and invertose may perhaps be likened to alloys; that is to say, they may be regarded as mixtures of definite compounds, combined in varying proportions.

CELLULOSE CHEMICALLY MODIFIED.

By S. FERNCEZI.

As far back as the seventeenth century various objects have been made of a mixture composed of paper pulp, gypsum, resin, or some similar substance. After this, paper and cardboard impregnated or covered with substances impervious to moisture, such as resins, wax, asphalt, varnish, &c., have been used for covering walls and roofs. But in every case the vegetable cell, though destroyed, retained its original physiological properties. In this article we propose to deal with products, the preparation of which necessitates the more or less complete destruction of the vegetable cell of the raw material by means of chemical reagents, the final result being an amorphous mass fit for industrial treatment.

I. *Parchment Paper*.—When unsized paper is dipped into sulphuric acid at 30° B., and the excess of acid

eliminated by washing and neutralisation, we obtain parchment paper, a product impervious to water, and resembling true parchment prepared from the skins of animals. The outsides of the cells become softened and unite to form a compact amorphous mass. Several kinds of parchment paper can be produced, this diversity depending on the composition and thickness of the raw material employed.

II. *Temporary Popularity of Parchment Paper.*—Thirty years ago sulphitic cellulose became the most important substance in the manufacture of paper, and it was soon recognised that when saturated for a long time in a pulping machine, it formed a viscous mass from which, from the point of view of transparency and impermeability to water and fatty bodies, a parchment paper could be prepared. It is supposed that here also, as in the case of parchmentised paper, a portion of the finely divided cellulose is transformed into hydrocellulose, but there is nothing to prove that this supposition is correct. As the price of this material is only half that of true parchmentised paper, it has supplanted this latter, and is almost exclusively used for packing perishable articles, such as food stuffs. The very thin, vitreous, transparent varieties are known commercially under the name of "pergamyn," and are used for packing goods of superior quality. To estimate the quality of this paper, above all its impermeability to fatty matter, recourse is had to what is called the "blister" test; the paper is held vertically over the flame of a candle, the quality is good if, before the paper commences to burn, a number of small blisters are formed very close to one another. To distinguish the old from modern parchment paper, it is submitted to mastication; the old kind gives a fibrous mass with short fibres; while true parchment paper gives a more or less hard mass, in which the presence of fibres cannot be detected.

III. *Cellulose.*—When the trituration of sulphitic cellulose is carried to an extreme so as to completely destroy the textile fibres, and to transform it into a uniform amorphous pulp, and this pulp is allowed to evaporate spontaneously, we obtain blocks of amorphous cellulose. This product has been named "cellulith;" the operation lasts, according to the nature of the cellulose used, from 40 to 150 hours. The cellulose, in a state of very fine division, entangles a large quantity of air, the presence of which might have a deleterious effect. For this reason it is advisable to remove the air either by means of a jet of steam, or by boiling the cellulose pulp briskly for an hour or two; the colouring matter, soluble or insoluble, should be added before this operation, when a coloured cellulith is desired. Cellulith can be worked like horn, ebonite, and similar substances. This new product is very suitable for the manufacture of valves; it resists the action of alcohol, petroleum, fats and oils, and is fairly elastic.

IV. *Vulcanised Fibre.*—Sulphuric acid of a given concentration is not the only agent which transforms cellulose into an amorphous mass; chloride of zinc and ammoniacal oxide of copper, in concentrated solution, act in the same manner. This property of chloride of zinc has already been put to profitable use since 1878 in the United States, for the manufacture of hard cardboard impervious to water, and for some years a factory has existed in Germany for the fabrication of vulcanised fibre. The manufacture of these products rests on the joining together by pressure of sheets of parchmentised paper, for which chloride of zinc is used in preference to sulphuric acid, since the least trace of any of this latter remaining between the layers would cause destruction of the material. The treatment with chloride of zinc is very difficult and complicated, especially if it is desired to obtain cardboard of 10 m.m. in thickness. Thin unsized paper is dipped in a solution of chloride of zinc of a known strength and at a given temperature. After removing the excess of the reagent the mass obtained is submitted to the action of suitable pressure until it is of the required thickness. It is washed and then exposed for some weeks to the action of the wind and rain; this appears to be an

important factor in the conversion of cellulose into hydrocellulose; it seems to be indispensable if great thickness is required of sufficient hardness and durability; it is then washed a second time. Commercially two kinds of vulcanised fibre are known, the flexible and the hard. The first can be very advantageously used in the manufacture of valves, pipes for the conduct of acids, alkalis, and gases; in a word, it can be used to replace indiarubber and leather. The hard modification is made not only in the form of sheets, but also in tubes, rods, &c.; and it can be sawed, turned, polished, &c., and is manufactured either in red, grey, or black, and is one of the worst conductors of electricity. For some time past vulcanised fibre has been used for the manufacture of cogged wheels; they run very smoothly and without noise.

V. *Celluloid.*—The treatment of cellulose by a mixture of concentrated sulphuric acid and fuming nitric acid gives rise to the formation of nitrocellulose, which is the starting point for the higher explosives; we shall not here, however, treat of this question. Another application of nitrocellulose is worthy of attention, that is its use in the manufacture of celluloid, a body which lends itself to the most varied uses. According to the method adopted by Hyat Brothers, the acid mixture falls in small drops on to a sheet of paper, which is slowly unrolled; this sheet is washed until all trace of acid has disappeared, is dried, cut up, and ground, and then intimately mixed with camphor. The plates thus prepared begin to soften at 80°, and at 125° they become plastic and malleable, so that they can be given any desired form. When heated to 190°, celluloid loses its transparency, and at a higher temperature it decomposes, giving off a reddish smoke. Although the addition of camphor has diminished the explosive force of the mixture, celluloid is nevertheless extremely inflammable, and contact with a match is sufficient to cause a mild form of explosion. Celluloid is capable of most varied applications.

VI. *Pegamoid.*—A few years ago English manufacturers placed on the market articles imitating leather made from cotton and paper. These articles were waterproof, and could be given any desired colour. They were called pegamoid. The surface of pegamoid is covered with a material the composition of which is kept secret, but it is supposed to consist of celluloid made pasty, probably by the addition of some oil. All articles made of pegamoid have a smell of camphor, which confirms the presence of celluloid. Among the principal applications of pegamoid we may mention tents, trunks, portmanteaus, curtains, &c. Pegamoid tissue can be pressed better than leather; it costs less and lasts longer. Pegamoid paper is not affected by grease, so cannot be printed by means of any oily inks, unless first treated with a certain quantity of siccative and salts. As the sun and rain have no action on pegamoid it can be used for permanent advertisements and for other outdoor purposes.—*Zeitschrift für Angewandte Chemie*, 1899, p. 51.

PROCEEDINGS OF SOCIETIES

CHEMICAL SOCIETY.

THE following are the abstracts of papers received during the vacation, and published in the *Transactions*:—

106. "*Researches on the Alkyl-substituted Succinic Acids. Part I. Methods of Preparation.*" By WILLIAM A. BONE and CHARLES H. G. SPRANKLING.

These acids may be prepared in quantity from the ethyl cyano-succinates produced by the interaction of ethyl cyanacetate and the esters of α -brom-fatty acids (*Proc.*, 1899, xv., 5).

An account is given of the properties of the ethyl

methylcyanosuccinates, the corresponding methylsuccinic acids, their characteristic anhydrides, anilic acids, and calcium salts.

107. "Some Derivatives of Dibenzyl Ketone." By FRANCIS E. FRANCIS, B.Sc., Ph.D.

Following R. Schiff's work on the interaction of benzal-aniline and acetoacetic ester and similar ketones, three isomeric addition products were obtained when dibenzyl ketone was employed. The first is produced by the action of corresponding amounts of the ketone and benzal-aniline, the second when the reaction takes place in the presence of traces of piperidine, and the third by the action of a trace of sodium ethoxide on either of the addition compounds obtained in the preceding reactions. No colour reaction with ferric chloride is given by either the ketone or any of the three isomeric substances. Like dibenzyl ketone, desoxybenzoin when treated with benzal-aniline gives three substances corresponding to the above, but, unlike it, it gives a fourth with piperidine, which is much less soluble and possesses a much higher melting-point than the others. The oxime and hydrazone, and the compounds formed by the action of ammonia and aniline on monobromodibenzyl ketone, are described.

108. "Action of Light and of Oxygen on Dibenzyl Ketone." By EMILY C. FORTEY, B.Sc.

When dibenzyl ketone is exposed to air in presence of sunlight, partial decomposition takes place with formation of benzaldehyde, benzoic acid, and phenylacetic acid. After prolonged exposure of a sealed tube containing the ketone with oxygen, another reaction was found to have taken place, carbon monoxide and toluene being produced, together with a substance melting at 193—194°, and having a composition corresponding with the formula $C_{15}H_{13}O$. These products were also formed when dibenzyl ketone was exposed in vacuous tubes or tubes filled with carbon dioxide.

109. "The Vapour Pressures, Specific Volumes, and Critical Constants of Hexamethylene." By SYDNEY YOUNG, D.Sc., F.R.S., and EMILY C. FORTEY, B.Sc.

A specimen of hexamethylene obtained by fractional distillation from Galician petroleum was found to solidify, though not completely, in an ordinary freezing mixture. It was therefore still further purified by fractional crystallisation until the melting-point rose to 4.7°. The density of the liquid at 0°/4° was 0.79675, b.-p. 80.9°, at 760 m.m. The vapour pressures, specific volumes, and critical constants were determined; the latter are:—Critical temperature = 280.0°, critical pressure = 30252 m.m., critical volume of a gram. = 3.659.

110. "The Composition and Tensions of Dissociation of the Ammoniacal Chlorides of Cadmium." By WM. R. LANG, D.Sc., and ALBERT RIGAUT.

This paper gives the results of experiments on the compounds formed by cadmium chloride with ammonia. The compound formed by the action of liquid ammonia at a temperature of -70° has the formula $CdCl_2 \cdot 6NH_3$. This substance, heated to 100°, loses ammonia, becoming $CdCl_2 \cdot 2NH_3$, which is extremely stable, like the corresponding salt of zinc, and begins to decompose at 210°, whilst at 300° decomposition is still incomplete. By the action of a solution of ammonia the diammoniacal compound is always obtained; if the hexammoniacal and those intermediate are required, gaseous ammonia must be passed into the solution. The tensions of these compounds, at temperatures varying from 0° to 70°, were measured; they show that at 60° the hexammoniacal compound ceases to exist, and, consequently, for the possible penta-, tetra-, and tri-ammoniacal compounds, temperatures between 60° and 100° must be employed.

111. "The Aluminium-mercury Couple. I. Action of Sulphur Chloride on some Hydrocarbons in presence of the Couple." By JULIUS B. COHEN and FREDERICK W. SKIRROW.

It has been shown by Hirst and Cohen (*Trans.*, 1895,

lxvii., 826) that the action of the aluminium-mercury couple closely resembles that of aluminium chloride (Friedel and Crafts, *Ann. Chim. Phys.*, 1884, [vi.], i., 520). The authors find that the couple is capable of wide application both as a condensing agent and as a halogen carrier. Sulphur chloride (S_2Cl_2) acts vigorously on the aromatic hydrocarbons in presence of the couple forming the disulphides. *Diphenylene disulphide*, $C_6H_4:S_2:C_6H_4$, and *ditoluylene disulphide*, $C_7H_6:S_2:C_7H_6$, were prepared in this way.

Dixylylene disulphide yields, on distillation, xylyl hydrosulphide, a liquid with a low boiling-point. The corresponding cumene compound forms a crystalline sulphydrate, $C_9H_{11}SH$, m.p. 87—90°. A compound probably identical with this is obtained from pseudocumylene disulphide together with the sulphide, $(C_9H_{11})_2S$, m.p. 110—111°. The products obtained by the distillation of dicymylene disulphide are liquid, and consist of a mixture of the sulphide and hydrosulphide. Sulphur chloride also acts on heptane in presence of the couple; but the product could not be crystallised.

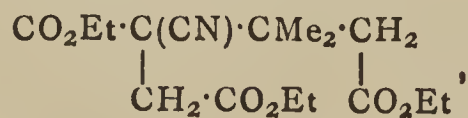
112. "The Aluminium-mercury Couple. II. The Action of Bromine on Organic Compounds in presence of the Couple." By JULIUS B. COHEN and HENRY D. DAKIN.

The aluminium-mercury couple may be used as a bromine carrier. In presence of small quantities of the couple, bromine forms substitution products with the aromatic hydrocarbons and with the paraffins, very satisfactory yields being obtained. The following substances were prepared in this way:—Bromobenzene, C_6H_5Br ; bromotoluene, C_6H_4MeBr ; bromo-*m*-xylene, $C_6H_3Me_2Br$; chlorobromobenzene, C_6H_4ClBr , from chlorobenzene; bromo-*p*-chlorotoluene, $C_6H_3MeClBr$, from *p*-chlorotoluene; *p*-dibromobenzene, $C_6H_4Br_2$, from bromobenzene; 1:2:4:5-tetrabromobenzene, $C_6H_2Br_4$, and hexabromobenzene, C_6Br_6 , from dibromobenzene; and dibromochlorotoluene, $C_6H_2MeClBr_2$, from bromo-*p*-chlorotoluene. Heptyl bromide, tetrabromoheptane, $C_7H_{12}Br_4$, and a third product, isomeric or polymeric with the latter, were obtained from heptane.

113. "Experiments on the Constitution of Isocamphoronic Acid." By W. H. PERKIN, jun., and JOCELYN FIELD THORPE.

During the course of experiments on the synthesis of isocamphoronic acid, the authors have prepared a substance of the constitution $CO_2H \cdot CH_2 \cdot CMe_2 \cdot CH(CO_2H) \cdot CH_2 \cdot CO_2H$, which Baeyer suggested as probably representing this acid, but they find that their synthetical acid is not identical with isocamphoronic acid.

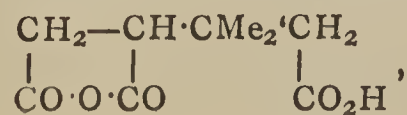
When the sodium derivative of ethyl cyanodimethylglutarate, $CO_2Et \cdot C(CN)Na \cdot CMe_2 \cdot CH_2 \cdot CO_2Et$ (compare *Trans.*, 1899, lxxv., 63), is digested with ethyl bromacetate, *ethyl cyanodimethylbutanetricarboxylate*,—



is obtained as a colourless oil which boils at 223—227° under 25 m.m. pressure. This ethereal salt, on hydrolysis with sulphuric acid, yields the *dimethylbutanetricarboxylic acid*, $CO_2H \cdot CH_2 \cdot CMe \cdot CH(CO_2H) \cdot CH_2 \cdot CO_2H$, represented above.

This acid has the very remarkable property of being apparently incapable of crystallising, as even when prepared by the hydrolysis of its pure ethyl salt—a colourless oil boiling quite constantly at 182—183° (22 m.m.)—or when set free from its characteristic calcium salt, it is always obtained as a thick colourless syrup. It thus differs widely from isocamphoronic acid, which crystallises with great facility.

When dimethylbutanetricarboxylic acid is distilled, it is converted into the corresponding *anhydro-acid*,—



a colourless oil which distils at 240—242° under 16 m.m. pressure.

114. "The *Cis*- and *Trans*- β -phenylbutane- $\alpha\alpha_1\alpha_2$ -tricarboxylic Acids." By JOCELYN FIELD THORPE and WILLIAM UDALL.

These acids, which are constituted somewhat analogously to the dimethylbutanetricarboxylic acid described in the preceding abstract, may be prepared as follows:—

In the first place, ethyl cinnamate is digested with the sodium derivative of ethyl cyanacetate, when combination takes place readily with the formation of the sodium derivative of *ethyl phenylcyanoglutarate*, $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CNa}(\text{CN})\cdot\text{CO}_2\text{Et}$. This compound reacts readily with ethyl bromacetate, yielding *ethyl phenylcyanobutanetricarboxylate*,—



This ethereal salt, which is a thick oil boiling at 270—280° (20 m.m.), is converted on hydrolysis into a mixture of the *cis*- and *trans*-phenylbutanetricarboxylic acids, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. The *trans*-acid crystallises from water in prisms containing $\frac{1}{2}\text{H}_2\text{O}$, but in the anhydrous condition it is a gum, with properties somewhat similar to those of the dimethylbutanetricarboxylic acid above described. The *cis*-acid melts at 178—180°, and is much more soluble in water than the *trans*-acid.

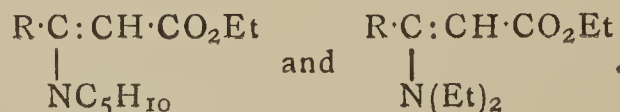
When treated with acetyl chloride, both acids yield the same anhydro-acid of the probable constitution—



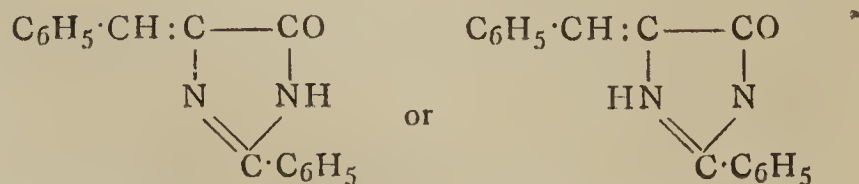
which melts at 134—135°.

115. "Further Studies on the Acids of the Acetylene Series." By SIEGFRIED RUHEMANN and ALFRED V. CUNNINGTON.

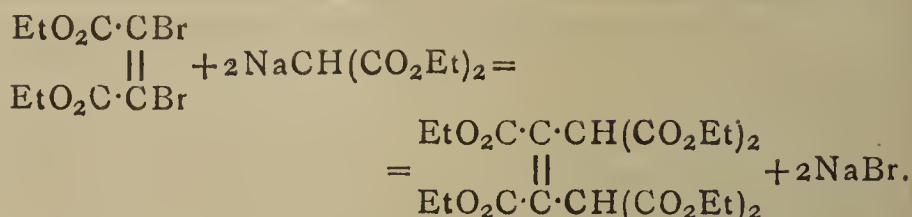
Ruhemann and Browning (*Trans.*, 1898, lxxiii., 723) have shown that the ethyl salts of unsaturated acids combine with piperidine, and that, in the case of ethyl phenylpropiolate, union takes place with great evolution of heat, Diethylamine does not combine with the salt until the mixture is heated to 100°, though like piperidine, it combines with ethylacetylenedicarboxylate very readily at ordinary temperatures. The compounds thus formed have the general formulæ—



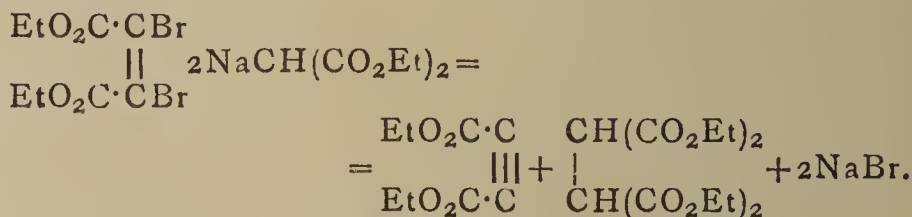
The authors further show that whilst urea and hydroxylamine react with ethyl phenylpropiolate, forming the ureide, $\text{C}_6\text{H}_5\cdot\text{C}:\text{C}\cdot\text{CONHCONH}_2$ (pale yellow needles, m. p. 220°), and the hydroxamic acid, $\text{C}_6\text{H}_5\cdot\text{C}:\text{C}\cdot\text{C}(\text{NOH})\text{OH}$ (colourless needles, m. p. 168—169°) respectively, benzamidine produces a cyclic compound (yellow needles, m. p. 274°), either—



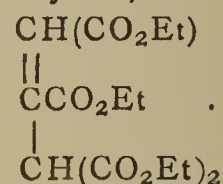
benzal-phenylglyoxalidone. They have also studied the additive products obtained by the action of bromine on ethyl phenylpropiolate and ethyl acetylenedicarboxylate (*i.e.*, ethyl dibromocinnamate and ethyl dibromomaleate respectively), and point out the remarkable difference in their stability. Ethyl sodiomalonate does not react with ethyl dibromocinnamate, but it does with ethyl dibromomaleate. This action, however, does not occur in the manner stated by G. Pum (*Monats.*, 1888, ix., 446), who supposed that ethyl dimalonylemaleate was formed according to the equation—



The authors prove that this substance is nothing but ethyl ethanetetra-carboxylate, which is produced thus:—



The ethyl acetylenedicarboxylate appearing in the equation unites with the ethyl malonate present and forms ethyl propenetetracarboxylate,—



This result shows that the substances obtained by Pum from his so-called ethyl dimalonylemaleate are the well-known products of the transformation of ethyl ethanetetra-carboxylate. His dimalonylemaleic acid is ethenyltricarboxylic acid, and his diglycolylemaleic acid appears, therefore, to be succinic acid.

116. "A Contribution to the Chemistry of the Mandelic Acids." By ALEX. MCKENZIE, M.A., D.Sc.

The work was undertaken in order to obtain *d*- and *l*-mandelic acids for the preparation of the optically active phenylalkoxyacetic acids recently described by the author (*Trans.*, 1899, lxxv., 753). Although recourse was eventually had to amygdalin as a convenient source of *l*-mandelic acid, the results with mandelic acid are given in view of the attention at present directed to the general subject.

Inactive mandelic acid was resolved on a large scale by use of quinidine and cinchonine. From the pure *d*- and *l*-acids so obtained, the salts of cinchonine, cinchonidine, quinine, quinidine, strychnine, brucine, and morphine were prepared, solubility determinations of which showed that the acid can be conveniently resolved into its optically active components by quinine, or, better, by morphine in alcoholic solution.

A number of metallic salts of the mandelic acids were prepared with the view of ascertaining whether any of them would lend themselves to separation by crystallisation. The attempts to obtain the separation of one enantiomorph by spontaneous crystallisations were unsuccessful, owing, the author supposes, to the "transition temperature" not having been reached, or to hemihedrism being absent or masked in the crystals of the active isomers.

117. "Non-existence of the so-called 'Suboxide of Phosphorus.'" By DAVID LEONARD CHAPMAN and F. AUSTIN LIDBURY.

The authors have examined specimens of the supposed suboxide, prepared by the methods of Goldschmidt and Reinitzer, and of Michaelis and Pitsch, and have compared their physical and chemical properties with those of red phosphorus in a finely divided state, prepared by the action of sunlight on a strong solution of phosphorus in carbon disulphide. They find complete coincidence of properties in both cases; and it is pointed out that no physical or chemical property has yet been observed by which these substances may be distinguished from one another. Analyses show that when purified as completely as possible, the percentage of phosphorus is greater in all cases than the formula P_4O demands; the impurities in the phosphorus being due chiefly to the presence of acids of phosphorus formed by the action of water during preparation.

They conclude that the so-called suboxide is only an impure form of red phosphorus.

118. "*The Chlorine Derivatives of Pyridine. Part III. The Interaction of Chlorine and Pyridine Hydrochloride.*" By W. J. SELL, M.A., F.I.C., and F. W. DOOTSON, M.A.

The authors have previously described a method of obtaining a considerable number of the chloropyridines (*Trans.*, 1898, lxiii., 432). With a view to simplifying the method of increasing the yield, they have examined the action of chlorine on pyridine hydrochloride, and succeeded in obtaining (1) a dichloropyridine not hitherto obtained by them, (2) a tetrachloropyridine, in large quantity, melting at 21–22°, (3) pentachloropyridine, (4) an aminotrichloropyridine, and (5) a compound of the empirical formula $C_{10}Cl_{11}HN_2$ and certain of its derivatives.

The substance (5), which is formed in considerable quantity, is regarded as being derived from two pyridine nuclei, and is still under examination.

119. "*Amidoamidines of the Naphthalene Series.*" By RAPHAEL MELDOLA and PERCY P. PHILLIPS.

The authors have continued the investigation of the ethenyltriamido-naphthalene described in 1887 (Meldola and F. W. Streatfeild, *Trans.*, li., 691). The acetyl and benzoyl derivatives are described, and the acid character of the NH-group of the amidine ring is made known by the formation of a silver compound and the corresponding N-methyl derivative. The diazotisable character of the NH_2 -group has been further studied, and it is shown that the amidoamine is also capable of combining with diazonium salts of other bases. The products do not appear to be simply diazoamido- or amido-azo-compounds as might have been expected from their mode of formation. The investigation of the latter is being continued.

PHYSICAL SOCIETY.

Ordinary Meeting, November 18th, 1899.

Prof. LODGE, F.R.S., President, in the Chair.

By invitation of Prof. Ayrton, this meeting was held in the Physical Laboratory of the Central Technical College.

Mr. F. S. SPIERS read a paper on "*Contact Electricity.*" The object of the paper was to determine in a more satisfactory manner than has hitherto been attempted the part played by the medium in the potential difference which arises when two dissimilar metals are put in contact. The first experiments were made with a piece of apparatus used by Professors Ayrton and Perry about twenty years ago. This apparatus, in which the metals in contact are capable of a rotation of 180° about a vertical axis, and are placed between two vertical inductors connected to a quadrant electrometer, was afterwards considerably improved, and the compensation arrangement of Lord Kelvin was introduced so as to measure the potential differences by a null method.

The metals first used were platinum and zinc, but, on account of the low melting-point of the latter metal, it was replaced by aluminium.

In order to try and remove the air sheets which cling to the surfaces of the metals, the tube was repeatedly heated and exhausted. The potential difference between the plates was found to gradually fall as this was done. It was proved that this was due to the oxidation of the aluminium, for, on cleaning its surface, the original effect was again obtained. Attempts were then made to remove the oxygen by displacing it with hydrogen; but, after four washings with pure dry gas and at low pressures, there was still enough oxygen left to completely oxidise the aluminium. The oxide of aluminium is not decomposed by hydrogen at a bright red heat. It was therefore decided to substitute iron and burn out the oxygen with hydrogen by encasing the lower part of the apparatus in a copper

tube and heating to bright redness with a blowpipe flame. By this means the value of the Volta effect between iron and platinum in an atmosphere of hydrogen was found to be 0.6 of a volt, the platinum being positive to the iron. This result is different both in magnitude and sign to that obtained when air is the medium.

The CHAIRMAN said he had given the subject of contact electricity some attention during the last fifteen years, and the author had performed a valuable series of experiments, which he should have liked to have seen done several years ago. He had always felt that a vacuum would never get rid of the condensed air films. The burning out process used had provided the most reliable results upon the subject.

Dr. LEHFELDT pointed out that the action of hydrogen upon ferric oxide was a limited one, and that it was impossible to bring about complete deoxidisation in that manner. At a dull red heat the ratio between the water-vapour and oxygen present is about 20 to 1.

Prof. PERRY expressed his interest in the experiments, but said that they had not affected his opinion upon the nature of the Volta effect.

Prof. ARMSTRONG said he was not wholly satisfied with the results, although a substantial approach to a solution had been made. The author had fully realised the difficulties of the experiments, but he had treated the matter as a surface gas effect, and had not guarded against moisture. Gases must be both dirty and moist before chemical action can take place, and we cannot expect to arrive at a solution of the problem until we have removed not only oxygen, but dirt and moisture. It is impossible to completely exhaust the apparatus, and a number of molecules must always be left which is more than necessary to produce the Volta effect; moisture can never be got rid of by exhaustion. The method of Dewar, of using liquid oxygen or liquid hydrogen would get rid of gases and water-vapour, and in this manner it would be possible to perform experiments which could be regarded as final. If the effect disappeared at low temperatures, it might be urged that the temperature was too low for it to be produced. The author must have been dealing with combination effects, for it had been proved that hydrogen alloyed both with platinum and iron at a dull red heat.

Mr. COOPER said he would like to see the experiments repeated after precautions had been taken to remove nitrogen from the apparatus.

Prof. S. P. THOMPSON said he had recently taken part in a discussion upon the subject with some earnest followers of the old contact theory. They uphold that the property of metals which determines the potential difference when two are put in contact is as fixed and definite as other physical properties, such as density; and that the potential difference observed in air is approximately the same as the true potential difference. It has been agreed to call the former the apparent potential difference. Prof. Thompson said that, according to Pellat, the real Volta effect was near to the effect observed in air. In circuits formed of metals there are other electromotive forces of the order of a millionth of a volt. The chemical electromotive forces in a circuit are of the order of a volt. The value of the Volta effect derived from thermodynamical considerations concerning the Peltier effect, is much smaller than observed chemical potential differences. If, however, we take into account, not only the Peltier effect, but also the Thomson effect, we will have other terms entering into the equations, which may tend to give a value more nearly equal to a volt. Prof. Thompson said that, in observing chemical E.M.F.'s, the Peltier effects did not come into the question, because of their smallness compared with the value of the chemical effect.

Prof. PERRY pointed out that the Peltier effect was not distinct from the Volta effect, but was simply the differential coefficient of it.

The CHAIRMAN said that if a circuit containing Peltier effects were treated thermodynamically, as if it were a

reversible heat engine, we could arrive at an equation connecting the value of the Peltier effects with the rate of change of the whole electromotive force in the circuit with temperature. The electromotive force which changed was not necessarily the Volta effect.

Prof. PERRY said he thought it was.

Prof. AYRTON suggested that an advance might be made in the theoretical side of the question if the Chairman were to put in writing his objections to the statement that the E.M.F. concerned was the true Volta effect. The extent of the Peltier effect proves the variation of the Volta effect with temperature; but because it is small it does not necessarily follow that the Volta effect is small. Where the Volta effect is a maximum or a minimum, the Peltier effect vanishes. The experimental work of the paper did not go far enough to convince him of the nature of contact electricity. Before we can hope to prove anything with respect to the two theories, we must be able to get a cyclic change of events; that is to say, we must be able to change our surfaces and media in a perfectly definite manner, so as to be able at any time to return to the particular state from which we started.

Prof. EVERETT said that as the variation in the potential difference between two metals in a medium was probably due to slow chemical action, which caused the metals to become less and less susceptible, he should expect that changing backwards and forwards from one medium to another would give to the potential difference an oscillatory variation, gradually becoming smaller and smaller.

The CHAIRMAN said he would like to see experiments showing a cyclic effect similar to that mentioned by Prof. Ayrton. The difficulty in these experiments is to avoid chemical action. Chemical action is not necessary to get the Volta effect. The effect would be greatest in dry gas; moisture tends to reduce the effect, and that is why its presence is unimportant.

Prof. CALLENDAR expressed his interest in the surface character of the effect, and its independence of the manner in which the plates were touched.

Dr. STANSFIELD suggested gold as a suitable metal to be experimented on, because of its non-oxidisability.

Mr. SPIERS, in replying, referred to Dr. Lehfeldt's assertion that the whole of the oxygen cannot be removed by hydrogen. In his experiments, however, there was very little ferric oxide and a large quantity of hydrogen, and although it was possible that all the oxide was not reduced, still a large portion of it was. The experiments were to be carried on, and attempts would be made to get a cyclic effect.

A paper on "The Heat of Formation of Alloys" was postponed until the next meeting.

CORRESPONDENCE.

DETERMINATION OF CARBON IN IRON AND STEEL WITHOUT ABSORPTION APPARATUS.

To the Editor of the Chemical News.

SIR,—I beg space in order to make some explanations necessitated by the criticism of H. Brearley (CHEMICAL NEWS, lxxx., 146) on my processes for the determination of "Graphitic and Combined Carbon in Iron" (*Iron Age*, May 11, 1899; CHEM. NEWS, lxxx., 121). In the first place, my title for the paper referred to ("Determination of Carbon in Iron and Steel without Combustion Apparatus") would have been more exactly and clearly stated if "Absorption" had been substituted for the word "Combustion."

I did not claim novelty for all the details of the processes; it would be well nigh impossible for any one to

present a new process that is novel from end to end. Though some of the details given are decidedly new as applied to the estimation of carbon, novelty is not what I was after. Until my article had been published, I had had no knowledge of any other chemist's previous investigations on the nature of the carbonaceous compound as deposited in copper solution, nor of their essays to make a direct determination of carbon on more or less similar lines of procedure; even since then, I fail to see that my processes have been wholly or largely anticipated, at least not to the extent of ensuring correct results.

The alleged differences between my figure for carbon (67.5) in the carbonaceous compound, and those decided on by the other investigators (70.96 by Schützenberger and Bourgeois, who described its composition as $C_{11}H_6O_3$; 72.7 by Zaboudsky, who wrote his formula $C_{12}H_6O_3$; and "about 70" by Blair in his book) are not so serious as they may seem to be, but, on the contrary, are small enough, since the carbon compounds experimented on were all prepared and obtained under more or less differing circumstances, and therefore were not exactly similar in composition. These variations would look insignificant when we remember what, in the early days of steel chemistry, were offered as the percentage of phosphorus in the dried phospho-molybdate precipitate; yet we to-day have a very accurate method of phosphorus determination by direct weighing of that precipitate. If Blair's formula for the carbonaceous residue was correctly quoted by my critic to be $(C_{50}H_{21}ClO_{15})_3 + O_2$, the percentage of carbon in it should be computed at 65.8 instead of "about 70," and this comes considerably within hailing distance of my figure. It is creditable to Mr. Brearley to have been able to dig up those prior investigations by the other chemists with their formulæ given. I feel sincerely obliged to him for the light of history that has been thrown on the matter, and also because the result of it has practically sustained my position. The factor of 67.5 is not theoretical, but actual, having been standardised by three standard steels of different grades of carbon which have been carefully determined by the regular combustion process. If the carbonaceous compound were soluble in warm dilute nitric acid, as claimed by some, how is it that the factor is only 67.5 instead of much higher, in order to compensate for the alleged loss? It is most important to eliminate copper sulphide and phosphide, which are most usually present in too appreciable quantity in the residue; this is accomplished by washing with warm nitric acid of the dilution recommended. Another requisite to the use of this factor with safety is to stir constantly, or very frequently, while dissolving drillings in copper solution. Never let the work of dissolving be interrupted overnight; else the black precipitate will be apt to have an irregular composition, as my experience has shown. It may be well stated that the golden rule to obtain success in all standardised processes of analysis is to operate under uniformly similar circumstances and conditions. This factor (67.5) applies to pig-iron and steel only; for ferromanganese, for instance, would require a much higher figure, about 80 or 90, depending on mode of operation, acidity, &c., as already announced in my previous paper.

The standard combustion method has a multitude of sources of error to be guarded against; indeed, eternal vigilance is the price of reliable determinations by that method. Dr. Dudley and others have put much stress on the difficulty of weighing correctly, or under exactly similar conditions, the absorption bulbs before and after the combustion, especially in damp weather. This is not surprising, seeing that the absorption apparatus is a bulky affair, and has an enormous amount of surface for the surrounding atmosphere to affect. It is not usually safe to weigh the apparatus until it has been in the balance case about half an hour, or, according to the opinion of the then head chemist of a large steel company in the city, not less than one hour. Some chemists have got so disgusted with this annoyance that they prefer to absorb the CO_2 in barium hydrate and weigh or titrate excess of

alkali. Arnold, in his "Steel Works Analysis," gives an instance of undue increase of weight of his bulbs by the absorption of SO_3 from the high sulphur contents of the carbon residue. Blair asserts that the dehydrating or dechlorinating power of anhydrous copper sulphate deteriorates rapidly, and it must be replaced after every two or three combustions if I remember aright. Langley advises that certain chlorine compounds, sure to be evolved during the combustion, be arrested by sodium oxalate or pyrogallate; Dudley uses a roll of metallic silver and acid ferrous sulphate to catch chlorine, and silver sulphate to take down HCl and chlorine compounds. The latter chemist also has an auxiliary furnace to pre-heat his oxygen gas, because it is often impure as bought in the market. Auchy demonstrated that potash solution of the usual density, 1.27 sp. gr., did not absorb CO_2 as completely as that of 1.41 sp. gr. would. Frequently has the claim been made with some plausibility that the platinum tube is permeable to gases at a red heat. Still, "there are others" to enumerate.

It may not be out of place here to call attention to the results of the considerable number of analyses made by different chemists in the States recently, on drillings from the same piece of iron. I shall give only results for combined carbon, seven determinations by colour, eight by oxidation with sulphuric and chromic acids, eight by combustion in Pt tube and weighing KHO bulbs, and two by combustion in Pt tube absorbing CO_2 in baryta and igniting and weighing, tabulated as follows:—

By colour.	By oxidation with H_2SO_4 and CrO_3 .	By combustion in a Pt tube.	
		Weigh KHO bulbs.	Absorb CO_2 in Ba hydrate. Ignite and weigh.
0.38	0.43*	0.56	—
0.45	0.44	0.91	—
0.52	0.51*	0.36	—
0.48	0.45*	0.52	—
0.35	0.47	0.57	—
0.40	0.45*	0.29	—
0.41	0.45	0.40	0.56
—	0.46	0.35	0.62
Av. 0.43	Av. 0.46	Av. 0.49	Av. 0.59

* By one and the same party.

The foregoing results by dry combustion do not by any means reflect credit on this standard method, though performed by supposedly past masters in their profession, even after making due allowance for accidental errors or irregularities in the sample, both of which are bound to occur occasionally. This table, it will be noted, gives considerable food for serious reflection. I have since received a small sample of that particular iron, and obtained 0.41 per cent combined carbon by colour, and 0.44 per cent by my process after dissolving in the cold, and 0.48 per cent after dissolving at a gentle heat. In my method 1 grm. of material is taken, whereas in the usual combustion or oxidation processes at least 3 or 5 grms. are required in order to minimise incidental errors by division (and frequently do not).

I am still of the opinion that the method I described for graphite also leaves very little to be desired for simplicity, rapidity, and accuracy, and is really to be preferred over any of the absorption processes in a great majority of cases; it is applicable in all cases where the metal is decomposable by dilute nitric acid. The proof of the pudding is in the eating.

The Gooch crucible, which is the essential part of both my processes, may be cheapened considerably by having it of porcelain with open bottom for a perforated platinum disc, and jacketed with thin platinum foil in lieu of the usual platinum cap for use in ignitions.—I am, &c.,

GEORGE T. DOUGHERTY.

Laboratory of the Sargent Company,
Chicago, U.S.A. Oct. 25, 1899.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 17, October 23, 1899.

Simultaneous Phenomena of Oxidation and Hydration under the Combined Influence of Free Oxygen and Light.—M. Berthelot.—The author previously investigated the relation between certain oxidising reactions and certain hydrating reactions. Certain oxidations take place under the simultaneous influence of oxygen and light. The present research investigates further to discover whether, acting on ethylic ether—one of the most simple types of compounds split up by hydration—this substance is susceptible at the same time of hydration; that is to say, changing a portion of itself into alcohol, and at the same time oxidising another portion.

Determination of the Coefficient of Solubility of Liquids.—A. Aignan and E. Dugas.—The authors have already determined this coefficient for two liquids which do not mix in all proportions when the temperature is constant and the liquids do not react upon one another. The present paper contains an account of the determination of the coefficient of solubility of two liquids which do not combine, and where there is a contraction of volume after agitation. The initial conditions of the experiment are as follows:—One of the liquids dissolves in the compound, and the excess of this non-combined liquid dissolves to saturation the compound formed. The determinations were made for aniline and water, and for amyl alcohol and water.

Journal de Pharmacie et de Chimie,
Series 6, Vol. x., No. 1.

Poisoning by Formol.—M. André.—Of late years, owing to the results of bacteriological experiments, formol has gradually come to be used in medicine, and also as a disinfectant. The author describes a case in which a patient took by mistake a spoonful of formol instead of another medicine; formol is a very irritant corrosive poison, and quickly destroys the skin and mucous membrane, besides having a very strong toxic effect. The best and quickest antidote has been found to be spirit of mindererus (acetate of ammonia), which quickly neutralises and decomposes the formol. This treatment, followed by an emetic, was found to be very efficacious, and in two days' time the patient had quite recovered.

Analysis of Gaseous Lemonades.—M. Frehse.—This paper contains the results of a number of analyses of lemonades, all of which were acidulated with tartaric acid; some were sweetened with saccharose and some with glucose. Of thirty-one manufacturers, one used glucose and saccharine together, two replaced a certain quantity of sugar with saccharine, and another added saccharine to increase the flavour of the lemonade.

Action of Dissolved Iodide of Potassium on Mercurous Iodide.—M. François.—Already inserted.

The Estimation of Chlorine, Bromine, and Iodine Mixed.—J. Bougeault.—Already inserted.

No. 2.

Volumetric Estimation of Aniline by Bromine and Bromine by Aniline.—G. Denigès.—Already noticed in this column.

Presence in the Animal Organism of a Soluble Ferment Reducing Nitrates.—E. Abelous and E. Gerard.—The authors show that in most animal organs, though in unequal proportion, there exists a soluble sub-

stance which reduces nitrates. From the facts observed, more particularly under the influence of varying temperatures, it appears probable that this substance is of a diastasic nature.

Clinical Estimation of Urinary Albumenoids.—G. Denigès.—Not suitable for abstraction.

Remarks on the Action of Heat on Pepsine.—V. Harlay.—The author's experiments show that the prolonged action of heat acts in diminishing the activity of the ferment. On the other hand, it is seen that the temperature which destroys pepsine in aqueous solution is about 68°; and at lower temperatures, even at 60°, pepsine undergoes a weakening action. Pepsine, however, appears to be able to resist the action of heat better in simple aqueous solution than in physiological solution; in the latter case the critical temperature is from 55° to 60°.

Detection of Formic Aldehyde in Milk.—Al. Leys.—Although a considerable number of reagents have been proposed for the detection of formic aldehyde, it has frequently happened that, in the case of searching for it in milk, only negative results have been obtained. It is, of course, present in only infinitesimal doses—one five-thousandth being sufficient to preserve milk for one hundred hours at a temperature of 25°. Bisulphite of rosaniline, made according to Schiff's formula, has especially been found to be untrustworthy. One solution only of this class has been found of real practical use by the author; it consists of 1000 c.c. of an aqueous solution of fuchsine at 1/1000th; 10 c.c. of bisulphite of soda at 30° B.; and 10 c.c. of pure concentrated hydrochloric acid. The bisulphite is added to the solution of fuchsine, and when the colour becomes very feeble the acid is added; after a few days the solution becomes perfectly colourless. The test is performed by distilling 100 c.c. of the milk; when about 20 c.c. has come over, a small quantity of this solution is added. If the milk is free from formic aldehyde, the solution remains colourless, even after several days; if, however, only 1/500,000th part of the latter is present, the solution takes an intense reddish violet colour after the lapse of a few minutes; even one-millionth part gives a distinct colouration. A solution of phloroglucine and potash-lye is also a very delicate reagent. If the milk is pure, the solution takes a pale green semi-transparent appearance; if, however, 1/100,000th part of formol is present, a brilliant—though fugitive—salmon-pink colour is produced; the colouration may also be noticed with only 1/1,000,000th part of formol present.

On a Chloro-iodide of Tin.—C. Lenormand.—Already inserted in full.

MEETINGS FOR THE WEEK.

MONDAY, 20th.—Society of Arts, 8. (Cantor Lectures). "Enamelling upon Metals," by Henry Hardinge Cunyngname.
WEDNESDAY, 22nd.—Society of Arts, 8. "National Forestry," by D. E. Hutchins.
THURSDAY, 23rd.—Society of Arts, 4.30. "Old and New Colombo," by John Ferguson.

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THE CHEMICAL NEWS.

VOL. LXXX., No. 2087.

A BIBLIOGRAPHY OF STEEL-WORKS ANALYSIS.

By HARRY BREARLEY.

(Continued from p. 234).

MANGANESE (continued).

II. SEPARATING OTHER ELEMENTS FROM MANGANESE.

33. *Aluminium*.—ROSE (C. N., ii., 266).—Add $(\text{NH}_4)\text{Cl}$, boil, add ammonia and boil off excess. Precipitate perfectly free from Mn.
34. *Nickel and Cobalt*.—TERRIEL (C. N., xiii., 133).—Permanganate completely precipitates manganese from ammoniacal solutions.
- 34a. JANNASCH and FRANZEK (Z. I. S. I., 1892, i., 493).—Solution of the sulphates converted to double cyanides and Mn precipitated with H_2O_2 . Re-precipitation recommended (Z. C. S., lxx., ii., 548).
35. *Nickel, Cobalt, and Zinc*.—GIBBS (C. N., xi., 148).—Precipitates in acetic solutions with H_2S .
CLARK (Z. C. S., lxiii., 1082).—Soda peroxide precipitates Mn from ammoniacal solutions free from Zn. Re-precipitation is required in order to separate Ni and Co.
TAMM (C. N., xxvi., 37).—Mn is precipitated with $(\text{NH}_4)_2\text{CO}_3$ free from Ni and Zn.
36. *Zinc*.—JANNASCH and NIEDERHOFHEIM (C. N., lxx., 159).—A mixture of KCN and KHO are added until precipitate is re-dissolved. Mn precipitated with H_2O_2 .
- 36a. RENARD (C. N., xx., 35).—Mn precipitated with soda phosphate and ammonia.
- 36b. BAYLEY (Z. C. S., liv., 388).—Zn precipitated with H_2S from a solution containing free phosphoric acid.
Separations with H_2O_2 .—Mn is separated from a number of elements by adding the mixture to an alkaline solution of H_2O_2 ; the procedure is very similar in each case. The references are:—
37. *Mercury*.—JANNASCH (C. N., lxxii., 65; and Z. C. S., lxviii., ii., 332).
38. *Silver*.—JANNASCH and KAMMERER (C. N., lxxii., 91; and Z. C. S., lxviii., ii., 423).
39. *Arsenic*.—JANNASCH and KAMMERER (Z. C. S., lxx., ii., 221).
40. *Chromium*.—JANNASCH and CLOEDT (Z. C. S., lxx., ii., 222).
41. *Zinc*.—JANNASCH and CLOEDT (Z. C. S., lxx., ii., 220 and 546). Also JANNASCH and MACGREGORY (Z. C. S., lx., 963).
42. *Copper*.—JANNASCH (Z. C. S., lxx., ii., 546).
43. *Copper and Cadmium*.—JANNASCH and ROTTGEN (Z. C. S., lxviii., ii., 331).
44. *Tungsten*.—TAGGART and SMITH (C. N., lxxv., 26).—Neither digestion with ammonium sulphide and $(\text{NH}_4)\text{Cl}$ nor with K_2CO_3 effects a complete separation.
45. *Phosphorus*.—GRANGER (C. N., lxxv., 95).—Fuse with KHO, evaporate acid solution to dryness, re-dissolve, and precipitate with ammonium sulphide.
46. *Chromic Acid*.—BREARLEY (C. N., lxxvii., 131).—Sodium carbonate added to cold solution, and filter at once or after heating to boiling-point. Precipitation with soluble phosphate, using considerable excess, in ammoniacal solution.
47. *Copper*.—KNORRE (Z. C. S., lii., 530).—To acid solu-

tion of sulphates or chlorides add nitroso- β -naphthol in acetic acid. Cu is precipitated.

III. GRAVIMETRIC ESTIMATION OF MANGANESE.

a. As Mangano-manganic Oxide.—

48. EGGERTZ (C. N., xviii., 232).—Precipitate with Br, wash with cold 1 per cent HCl, dry at 100°C ., and weigh as hydrated oxide (59.21 per cent Mn), or ignite to Mn_3O_4 .
49. KESSLER (C. N., xxvii., 14).—Precipitates with Br and sodium acetate.
50. ABEL (C. N., vi., 125).—Precipitates Mn from ammoniacal solution with bromine.
51. PIESSE (C. N., xxix., 110).—Precipitates with Br and ammonia, and allows to stand eighteen hours.
52. WILLIS (C. N., xxix., 150).—Uses more Br and ammonia, and points out that the precipitation of the Mn is immediately complete.
53. RIGGS (Z. C. S., lxii., 536).—Bromine should be added to the hot ammoniacal filtrate.
- 53a. MÜLLER (Z. I. S. I., 1886, 392).—Acetate separation of Fe. Precipitates Mn with H_2O_2 and $(\text{NH}_4)\text{HO}$, and ignites.
54. MEINECKE (Z. I. S. I., 1887, i., 469).—ZnO separation of Fe; filtrate mixed with HgO ; heat to boiling-point and precipitate with Br. The precipitate is washed with dilute HNO_3 (free from nitrous) and ignited.
55. JUPTNER (Z. I. S. I., 1885, 247).—Precipitated sulphide dissolved in acetic acid, evaporated, and ignited to Mn_3O_4 .
56. KERN (C. N., xxxii., 100).—Fe and Mn precipitated with KHO, heated in H; mixture powdered under naphtha oil; Fe separated with magnet, and MnO ignited to Mn_3O_4 .
57. PARKER (C. N., xxii., 186).—Spiegels contain Cu up to 0.5 per cent; this is precipitated by the Br and ammonia, and to some extent if Mn is precipitated as phosphate.
58. MATHESIUS (C. N., liii., 74).—Oxides of Mn ignited along with NH_4Cl are partly volatilised. (See 17).
59. PICKERING (C. N., xliii., 189).—The degree of oxidation of MnO_2 . MnO -compounds is influenced by heating in air at 100°C ., or even by boiling in water. Compounds variously oxygenated are produced when oxides of manganese are heated to redness in a platinum dish over a Bunsen. Permeability of the platinum probable cause of the error.
60. PATTINSON (Z. C. S., lxii., 536).— Mn_3O_4 formed only by ignition at almost white heat, the oxide being protected from reducing agents; heat of a Bunsen not sufficient to form Mn_3O_4 ; heating over gas blowpipe dangerous, owing to reducing gases permeating the crucible. All ignitions in air need confirmation by a determination of the available oxygen.
61. GORGEU (Z. C. S., liv., 653).—After heating to bright redness, Mn_3O_4 absorbs absolutely no oxygen on cooling.
62. MEINECKE (Z. C. S., lvi., 311).—To prevent the ignited precipitate containing fixed alkali, it should be heated with $(\text{NH}_4)\text{Cl}$ and ammonia before filtering.
63. GOOCH and AUSTIN (C. N., lxxvii., 255).—Ignition to Mn_3O_4 may be made in strong Bunsen or blast-lamp in such a way that an oxidising flame covers the entire wall of the crucible.

III.b. Estimation of Mn as Pyrophosphate.—

64. GIBBS (C. N., xvii., 195).—Describes the precipitation as ammonium-manganese phosphate. Refers to other metals precipitable as ammonio-phosphates.
65. GOOCH and AUSTIN (C. N., lxxviii., 239).—The success of the precipitation depends mainly on the change of $\text{Mn}_3\text{P}_2\text{O}_8$ to NH_4MnPO_4 ; the presence of $(\text{NH}_4)\text{Cl}$ or a substitute essential to completeness

of this change; the proportion $(\text{NH}_4)\text{Cl}$ to final $\text{Mn}_2\text{P}_2\text{O}_7$ should be at least 50 to 1; large excess not harmful; ammonia used in slight excess; glass vessels available if operation is rapid.

66. MCKENNA (*C. N.*, lxiii., 184).—Compares Gibbs's original process (64) and Blair's ("Chem. Anal. of Iron") modification. The precipitate must be quite crystalline; a trace of Mn always found in the filtrate; hot water, $(\text{NH}_4)\text{HO}$, and $(\text{NH}_4)\text{NO}_3$ all slightly dissolve the precipitate; glass vessels may be used.

III.c. Estimation of Mn as Sulphate.—

67. GOOCH and AUSTIN (*C. N.*, lxxvii., 256).—Estimation as sulphate formerly recognised procedure; definite condition of hydration thought hard to attain to. Volhard used a ring burner in iron casing, and obtained excellent results; authors support crucible on a triangle within a larger crucible, and are able to heat the outer one to redness without risk; good results; regarded as most reliable of the gravimetric processes.

III.d. Estimation of Mn as Sulphide.—

68. ROSE (*C. N.*, ii., 302).—Precipitated sulphide not wholly insoluble, especially in liquids containing ammonia salts; the precipitate is deposited slowly.
69. BLUM (*J. I. S. I.*, 1890, i., 372).—In presence of Ca the precipitation should be made in boiling solutions and rapidly filtered, as calcium hyposulphite may crystallise out.
70. FRESSENIUS (*C. N.*, iv., 150).—Ammonium sulphide does not precipitate very dilute solutions of Mn; $(\text{NH}_4)\text{Cl}$ favours the precipitation after some time.
71. MEINECKE (*J. C. S.*, liv., 1132).—Precipitated from boiling solutions containing excess of ammonia; a trace remains unprecipitated; large amounts of $(\text{NH}_4)\text{Cl}$, NaCl , or $\text{NH}_4(\text{C}_2\text{H}_3\text{O}_2)$ are without influence. Satisfactorily separates Ca and Mg.

III.e. Precipitation of Mn as Carbonate.—

72. FORBES (*C. N.*, xvi., 105).—Precipitates with sodium carbonate.
73. TOSH (*C. N.*, xvi., 168).—Re-dissolves precipitated sulphide in HCl , precipitates with sodium carbonate, and ignites to Mn_3O_4 .
74. TAMM (GUYARD) (*C. N.*, xxvi., 37).—Precipitates with ammonium carbonate; claims this, amid much rattle, as a startling discovery. Allen (*C. N.*, xxvi., 81, speaks of it as an old process.
75. AUSTIN (*C. N.*, lxxvii., 242).—Precipitation as carbonate complete; presence of $(\text{NH}_4)\text{Cl}$ necessary to ensure filterable precipitate. Preferable to weigh as sulphate.
76. GORGEU (*C. N.*, lix., 277).—At the common temperature carbonate or oxide of Mn cannot absorb from air or aerated water a proportion of O greater than corresponds to $\text{MnO}_2\cdot\text{MnO}$.

III.f. Estimation of Manganese Electrolytically.—

77. RICKE (*C. N.*, xxxvi., 90).—Deposited as peroxide. Cu, Ni, Co, Zn, Mg, Al, alkalis or alkaline earths, may be present. Large amounts of Fe injurious.
78. KAEPEL (*C. N.*, lxxvii., 201; and lxxix., 195).—Deposited partly as metal and partly as MnO_2 from neutral or faintly acid solutions; very strong current used; addition of acetone improves results.
79. VORTMANN (*J. I. S. I.*, 1892, i., 490).—Mn and Hg precipitated simultaneously as an amalgam; Zn, Pb, Cd, Sb, As, and Bi, which do not form coherent deposits, can be similarly estimated (see *C. N.*, lxiv., 227, &c.).
80. ENGELS (*J. C. S.*, lxxiv., ii., 52).—Deposited at 80°C . from solutions containing Cr alum, or alcohol and ammonium acetate.
81. BRAND (*J. C. S.*, lviii., 294).—After dissolving in pyrophosphate, MnO_2 is deposited, adhering firmly. Ignited to Mn_3O_4 .

82. RÜDORFF (*J. C. S.*, lxiv., ii., 94).—Mn should be present as sulphate; deposited hydrated peroxide dried at 60° and weighed.

83. CLASSEN (*J. C. S.*, lxvi., ii., 480).—Solution electrolysed in presence of acetic acid; peroxide ignited to Mn_3O_4 .

84. VOLMAN (*J. C. S.*, lxxiv., ii., 50).—Deposited from HNO_3 solution at 50° ; small current; solution in oxalate, acetic acid, or pyrophosphate do not give good results.

85. GRÖGER (*J. C. S.*, lxviii., ii., 419).—Electro-deposited Mn not entirely peroxide. Only 94 to 96 per cent estimated by KI and thiosulphate, on the assumption that the precipitate is MnO_2 .

III.g. Estimation of Mn (Miscellaneous).—

86. CARNOT (*C. N.*, lvi., 16).—Precipitated as vanadate from an ammoniacal solution. Ignited precipitate has the composition $2\text{MnO}\cdot\text{V}_2\text{O}_5$.

(To be continued).

NOTES ON A REMARKABLE CASE OF METALLIC CORROSION.

By E. T. ALLEN.

LAST June several boxes of analytical weights, of the make of Bender and Hobein, of Munich, were put away for the summer in an iron safe. The larger weights were of gold-plated brass, the smaller of platinum.

The weights had been in use in the laboratory for one year, and when put into the safe were in good condition. When taken out, after less than three months, the varnished boxes could only be opened by vigorous prising. Moisture had evidently found its way within, for the ivory points of the tweezers, and in some cases the velvet linings of the boxes, were white with mould. The platinum weights were as bright as new, but the top of every one of the gold-plated weights was covered with a white substance which could not be removed by either brushing or rubbing. An examination showed that these weights were abnormally heavy. By careful scraping of more than fifty of them, a small quantity of white powder was obtained, yet sufficient for several satisfactory qualitative tests. It proved insoluble in water, soluble in hydrochloric and nitric acids. The colourless nitric acid solution gave no precipitate with silver nitrate, proving that no halogen was concerned in the corrosion. The hydrochloric acid solution gave no precipitate with ammonia, but a white precipitate with ferrocyanide of potassium. The ammoniacal solution yielded a brownish white precipitate with ammonium sulphide.

Heating on platinum foil revealed the presence of organic matter, though apparently in fragments. On charcoal a white coating was obtained, and this with cobalt nitrate gave the characteristic Rinmann's green. The substance was therefore some compound of zinc—probably either the hydroxide mixed with mould or a zinc salt of some organic acid. Lack of material prevented a more complete examination. Since the weights were tightly boxed, and kept in a closed safe which contained no chemicals of any kind, the action can only be assigned to water and mould, which were certainly present. It is well known that plated metals at exposed points are more susceptible to corrosion than either metal alone, owing to electrolytic action. In such cases it is of course the more positive metal which is attacked. This is seen to be true in the above-mentioned case—the zinc is attacked, while the copper and gold are unaffected. That the brass should be reached through the plating seems remarkable, to say the least. A microscopic examination showed that wherever corrosion had touched the weights, the gold had become granulated or blistered. A case which seems to me to possess some points in common with this has

recently been described by Witter (*Berg. und Hütt. Zeit.*, July 28, 1899, p. 349). The amalgamated plates of a stamp-mill in Smaland, Sweden, were attacked by the water used, which had its source in a peat-bog. The plates became covered with a green slimy substance, which proved to be an organic compound of copper. It is notable that the more positive metal was attacked in spite of the layer of amalgam which protected it, and also that a piece of copper *alone*, after standing six months in the partly evaporated water, was unattacked.

This naturally raises the question, Are gold-plated weights, under ordinary working conditions, preferable to brass weights? Any new light on the subject would be gladly received.

State School of Mines, Rolla, Missouri.

THE DECOMPOSITION OF CARBONIC ACID IN THE PRESENCE OF CARBON.

By O. BOUDOUARD.

In a previous paper (*Bull. Soc. Chim.*, Series 3, vol. xxi., p. 465) I published the results arrived at in my research on the reaction $\text{CO}_2 + \text{C} = 2\text{CO}$, at a temperature of 650° . I have now continued this research at higher temperatures.

1. *Experiments at 800° .*—I used the same apparatus, with the porcelain tube, described in my preceding paper. The pumice impregnated with metallic oxide was replaced by fragments of carbon of the size of a nut. When the apparatus is filled with carbonic acid gas, the outer tap is closed and the other extremity plunged into mercury. As there will be an increase of pressure on account of the reaction $2\text{CO} = \text{CO}_2 + \text{C}$, the gas must be thus allowed to escape freely. The heat is applied for varying periods of time, when the gas is extracted and analysed. I have also made experiments in the presence of charcoal formed by the decomposition of carbonic oxide. The following results were obtained:—

Time. H. M.	Wood charcoal.		Retort carbon.		Coke.		Carbon from CO.	
	CO ₂ .	CO.	CO ₂ .	CO.	CO ₂ .	CO.	CO ₂ .	CO.
0 8	17.1	82.9	86.7	13.3	83.6	16.4	13.6	86.4
1 0	6.1	93.9	65.8	34.2	—	—	—	—
1 30	—	—	—	—	42.6	57.4	8.0	92.0
2 30	—	—	—	—	—	—	7.1	92.9
6 0	6.7	93.3	—	—	11.0	89.0	—	—
7 0	—	—	43.3	56.7	—	—	—	—
9 0	—	—	—	—	12.8	87.2	—	—
9 30	—	—	29.7	90.3	—	—	—	—

In another series of experiments I used charcoal in much smaller pieces, 2 to 5 m.m. diameter. The results obtained were as follows:—

Time. H. M.	Wood charcoal.		Retort carbon.		Coke.	
	CO ₂ .	CO.	CO ₂ .	CO.	CO ₂ .	CO.
0 8	39.9	60.1	80.1	19.9	79.1	20.3
1 0	9.9	90.1	41.2	58.8	39.8	60.2
1 30	10.1	89.9	—	—	—	—
6 0	6.3	93.7	17.2	82.8	15.6	84.4
9 0	—	—	12.7	87.3	—	—

The results are practically the same with wood charcoal and coke whether large or small fragments are used; with retort carbon there is an increase in the speed of the reaction, but the limit reached with wood charcoal and carbon from CO is not attained—at least, not after being heated for at least nine hours. Considering these figures as a whole, we see that in all the different cases the general phenomena are the same, there is only a difference in the speed of the reaction. The decomposition of the carbonic acid is not complete; but as at 650° , the limit reached at 800° is the same as that obtained in studying the decomposition of carbonic oxide (93 per cent CO and 7 per cent CO₂).

2. *Experiments at 925° .*—Experiments made with the same apparatus as those at 800° show that the quantity of carbonic acid remaining diminishes more and more; the measurements of their volumes becoming more and more difficult, I substituted the ponderable method for the volumetric. For varying periods of time, I passed a current of carbonic acid over carbon. At the escape tap of the apparatus the gaseous mixture was passed through a flask containing baryta-water. A check tube of baryta-water showed that the carbonic acid was completely absorbed. From the weight of carbonate of baryta thus obtained, the quantity of carbonic oxide formed was calculated.

1. *1.25 Litres of CO₂ Gas for Thirty Minutes.*—CO₂BaO obtained = 0.3765 grm.; corresponding CO₂ = 0.0838 grm., or 3.3 per cent (vol.).

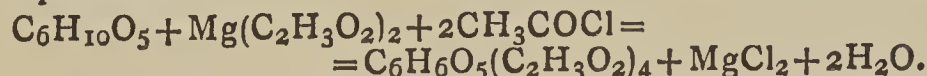
2. *3.5 Litres of CO₂ Gas for One Hour Thirty Minutes.*—CO₂BaO obtained = 0.1045 grm.; corresponding CO₂ = 0.3127 grm., or 4.5 per cent (vol.).

At a temperature of 925° there thus still remains in the gaseous mixture resulting from the reaction of carbonic acid on carbon a proportion of 4 per cent of carbonic acid.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 15.

THE PROGRESS MADE IN THE CELLULOSE INDUSTRY.

By Dr. C. O. WEBER.

WITHIN the last three or four years the domain of the industrial application of cellulose has been enriched by a new product, which constitutes the point of departure of a whole series of homologous bodies, some of which are certainly destined to play an important part from the industrial point of view. This is acetate of cellulose, prepared by a method discovered by Cross and Bevan. The originality of the process is represented by the following equation:—



The industrial importance of this process rests in the fact that only two acetyls are obtained from chloride of acetyl and at a high price, while the two others are prepared with acetate of magnesium, and with ordinary acid. It is supposed *a priori* that this same body, acetate of cellulose, can be obtained by the action of acetic anhydride on cellulose, for it is extremely probable that in the above reaction, there is first of all an action of the chloride of acetyl on the acetate of magnesium, with the formation of acetic anhydride. In reality we cannot effect the transformation of cellulose into the tetracetate by means of acetic anhydride; we can only obtain a tri-acetate with properties of no particular value. Even to effect this result such an enormous excess of anhydride must be used that the commercial production of this acetate would have no chance of success owing to the great expense involved.

The manufacture of tetracetate of cellulose by Cross and Bevan's process is already being carried on on a large scale, as is also the manufacture of tetrabutyrates of cellulose, prepared in an analogous manner.

Besides these ethers of cellulose, we at present know nothing beyond the nitrates of cellulose, which are distinguished from the former by their explosive properties. The ethers are not inflammable, and only burn imperfectly. With solvents they behave in the same manner as the nitrates, in so far that all their solutions are of a colloidal nature, but they differ from the nitrates with regard to the extent of their solubility. The acetate is completely insoluble in methylic and ethylic alcohols, acetate of ethyl, acetate of amyl, acetone, and ether; but, on the other hand, it is soluble in benzoate of ethyl, chloroform, epichlorhydrine, acetic anhydride, glacial acetic acid, and nitrobenzene. The solution of the acetate in this last

substance becomes on cooling a solid but completely transparent jelly. A fact to be noted is that the solutions of the tetracetate in chloroform, epichlorhydrine, or benzoate of ethyl can be diluted with acetone without the slightest precipitation taking place. When evaporated on a plate of glass, the solutions of the acetate leave residues in the form of particles or filaments of great transparency.

The acetate resists the action of reagents in a remarkable manner; dilute acids, with the exception of nitric acid, do not attack it at all, and the same is the case with alkaline lyes, even at a high temperature, while these reagents completely destroy the nitrates even in the cold.

When boiled for several hours with an alcoholic solution of soda, very fine particles are completely saponified, but the saponification does not disintegrate the material so that the particles retain their form and transparency.

The insulating properties of the acetate are also worthy of notice, properties which considerably surpass those of indiarubber and guttapercha.

The acetate is very durable and does not begin to soften below a temperature of 150° , and this change is not accompanied by any destruction of material.

The hydrate of cellulose is entirely analogous with the acetate, from the point of view of its chemical properties, its resistance to the action of reagents and to high temperatures; but it is more soluble than the acetate in the solvents mentioned above, and it is easily soluble in acetate of ethyl and in acetone.

The filaments prepared from the butyrate closely resemble those formed from the acetate, but they are a little more flexible and softer.

These properties clearly show the commercial importance of the acetate and the butyrate of cellulose, and it is certain that these substances will soon become powerful rivals of celluloid in certain of its applications. This will be especially the case when there is an advantage in using a non-inflammable material, in preference to one eminently inflammable. Further, on account of their non-inflammability, their resistance to the action of moisture and high temperature, and their high insulating properties, these cellulose ethers can easily replace mica and be employed as an insulator, &c. It is also certain that these bodies can be advantageously used as metallic lacquers, for their resistance to atmospheric influences render them unique in this respect; in fact, we can safely predict a prosperous future for the butyrate and acetate of cellulose.—*Zeitschrift für Angewandte Chemie*, 1899, p. 5.

THE CHEMICAL ANALYSIS OF ROCKS: ESTIMATION OF POTASSIUM AND SODIUM.

By ED. BONJEAN.

In a recent communication made to the Academy of Sciences (*Comptes Rendus*, cxxviii., May 1, 1899) by Michel Lévy, "On the Separation into Two Natural Groups of the Volcanic Overflow of Mont Dore; Distinctive Chemical Characteristics of their Magmas and of the Material which has Fed the Eruptions of the Puys Range" results of the analysis of eleven volcanic rocks obtained from the periphery of the crater of Mont Dore were given; the analyses were afterwards reproduced here. It was very important to determine exactly the respective quantities of soda and potash in these rocks. The following was the method used by preference, instead of any previously known one, after having proved the exactness of our method many times by the chemical analysis of waters and rocks. This process requires a good deal of time and care. Unfortunately the quantities of soda and potash cannot be exactly determined until after having completely isolated the salts of these two alkaline metals in a state of absolute purity.

Method of Analysis.

1. The silica was determined as well as the oxide of iron and aluminium; the lime, magnesia, and sulphuric acid after attacking the rock with alkaline carbonates.

2. The attack with carbonate of lime (1 grm. of rock to 0.5 grm. of carbonate of lime) was effected in a Forquignon-Leclerc furnace, for the estimation of the alkaline metals. The amount of silica is checked. As for the oxides of iron and aluminium, the lime, and magnesia, the results here obtained are generally incorrect, no matter what care may be used in the separation of these bodies, on account of the dissemination of the large quantity of lime added. The separation and estimation of the potash and soda are effected in the following manner:—The silica, oxide of iron, aluminium, and lime are eliminated in the ordinary manner. The remaining solution is evaporated to dryness on the water-bath, and the ammoniacal salts (oxalate, acetate, and chlorhydrate) are driven off by heat. Take up with water, and separate the magnesia in the form of ammonio-magnesian phosphate; this is the only manner in which it can be entirely got rid of. The ammonia is driven off, and the phosphate of ammonia precipitated by a fresh solution of pure neutral acetate of lead at 10 per cent in large excess. Filter and remove the excess of lead by means of sulphuretted hydrogen. After filtration and evaporation of the liquid on the water-bath, the residue is heated to dull redness, taken up with very dilute hydrochloric acid, filtered, and concentrated. The potassium is precipitated by chloride of platinum with alcoholic ether added. Filter, and wash with alcoholic ether; dissolve the chloroplatinate of potassium in warm water; displace the platinum by magnesium; filter, wash, incinerate, and weigh; the platinum precipitated corresponds to the potassium.

From the solution separated from the PtCl_4KCl , the alcoholic ether is driven off by heating, the platinum is precipitated with SH_2 while hot; this is then filtered, evaporated, and the residue brought to a red heat after the addition of sulphuric acid. This leaves sulphate of soda, which is weighed and can then be crystallised.

Chemical Analysis of Eleven Volcanic Rocks.

I. Phenolite from Roc Blanc.

II. Phenolite from Malvalle.

	I.	II.
SiO_2	58.70	54.97
Al_2O_3	22.36	25.84
Fe_2O_3	5.08	6.29
MgO	1.27	1.13
CaO	3.39	5.21
K_2O	5.45	3.52
Na_2O	5.13	4.49
SO_3	Traces	—
P_2O_5	—	Traces
	101.38	101.45

III. Trachyte in large crystals from Quenille.

	III.
SiO_2	56.36
Al_2O_3	21.32
Fe_2O_3	7.29
MgO	2.06
CaO	5.07
K_2O	3.65
Na_2O	6.17
SO_3	—
P_2O_5	—
	101.92

IV. Tephritic haüyne, below l'Aiguiller de Guéry (slightly decomposed).

V. Tephritic haüyne, between Quenille and Puy-Loup.

- VI. Tephritic haüyne, under the Roc Blanc.
VII. Tephritic haüyne, under the Roc Blanc (slightly decomposed).
VIII. Tephritic haüyne, under the Roc Blanc.

	IV.	V.	VI.	VII.	VIII.
SiO ₂	54'00	53'60	53'20	53'00	52'80
Al ₂ O ₃ . . .	24'10	22'57	24'16	22'63	21'95
Fe ₂ O ₃ .. .	8'95	6'78	7'07	7'50	10'96
MgO .. .	2'35	3'92	2'20	2'47	3'06
CaO .. .	4'65	5'80	6'38	7'14	7'05
K ₂ O .. .	1'58	4'01	3'21	5'89	2'39
Na ₂ O . . .	5'60	5'11	4'44	1'72	4'37
SO ₃ .. .	—	Traces	0'50	0'25	—
P ₂ O ₅ .. .	—	—	—	—	—
	101'23	101'79	100'16	100'60	102'58

- IX. Ophitic basalt, below Ordenche.
X. Basalt from Puy-Loup.
XI. Compact basalt from the summit of Ordenche.

	IX.	X.	XI.
SiO ₂	49'00	47'23	44'50
Al ₂ O ₃	21'70	24'25	21'50
Fe ₂ O ₃	13'30	11'33	14'90
MgO	5'22	4'85	7'60
CaO	8'95	8'47	8'96
K ₂ O	1'95	1'64	2'47
Na ₂ O	0'63	1'81	1'36
SO ₃	—	—	—
P ₂ O ₅	—	—	—
	100'75	99'58	101'26

—Bull. Soc. Chim., Series 3, vol. xxi., No. 14.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING OCTOBER 31ST, 1899.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To the Water Examiner, Metropolis Water Act, 1871.

London, November 10th, 1899.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 208 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Oct. 1st to Oct. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 208 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during October was 2'59 inches, of which 2'22 inches fell on four days, viz., the 1st, 26th, 27th, and 29th; the heaviest fall was on the 27th, when 0'9 inch fell. The average rainfall for this month is 2'75 inches; we thus find a deficiency of 0'16 inch, bringing the total deficit for the year up to 3'84 inches, or 18'1 per cent on the thirty years' average.

Our bacteriological examinations of 386 samples have given the results recorded in the following table; we have also examined 39 other samples, from special wells, stand-pipes, &c., making a total of 425 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	290
New River, filtered (mean of 78 samples) ..	10
Thames, unfiltered (mean of 26 samples) ..	1367
Thames water, from the clear water wells of eight Thames-derived supplies (mean of 204 samples)	20
Ditto ditto highest	341
Ditto ditto lowest	0
River Lea, unfiltered (mean of 26 samples) ..	876
River Lea, from the East London Company's clear water well (mean of 26 samples) . . .	21

The chemical and bacteriological analyses for the month show that the supply of water to the metropolis continues to be highly satisfactory.

Our attention has been drawn to the Report of the Proceedings of the London County Council for the 24th of October, where it is stated, on pp. 1433-34, that there exists a variation between the results of analyses made by the late Sir E. Frankland and ourselves. It is remarked that while Sir E. Frankland found the highest proportion of organic carbon during the month of July last in the water supplied by the Lambeth Company, our results showed the water of the Grand Junction Company to contain the highest average amount of organic carbon. We give here the actual figures:—

	Organic Carbon in parts per 100,000.	
	Sir E. Frankland. (One analysis).	Ourselves. (Mean of 4 analyses).
Lambeth	0'123	0'123
Grand Junction (Kew) ..	0'118	0'134
Grand Junction (Hampton)	—	0'126

Again, in the same Report, it is said that in August Dr. Percy Frankland found the highest proportion of organic carbon in the Lambeth and Chelsea waters, while we found the highest average amount in the water from the Southwark and Vauxhall Company. Here also we give the actual figures:—

	Organic Carbon in parts per 100,000.	
	Dr. P. Frankland. (One analysis).	Ourselves. (Mean of 4 analyses).
Lambeth	0'118	0'128
Chelsea	0'118	0'120
Southwark and Vauxhall..	0'110	0'130

We must point out that the above figures are remarkably concordant, the variations being confined to the second and third places of decimals; the actual variations between our respective results being less than one part per million. So close an agreement between different chemists on samples taken on different days is very striking, and instead of the figures being characteristic of any discrepancy, they are practically identical, considering the nature of the analysis.

The statement on p. 1434 of the above-quoted Report, that our samples for chemical analysis are taken from the Water Companies' clear water wells, is inaccurate. Our Reports state that the samples are taken from the Companies' mains in various parts of London, some of them being drawn from the identical stand-pipes whence Sir E. Frankland's samples were taken.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

THE VARIATION IN THE COMPOSITION OF "PARIS GREEN," WITH SCHEME FOR ANALYSIS.*

By THOMAS B. STILLMAN, Ph.D.

THE increasing consumption of Paris green (also called Schweinfurt green, French green, Mitis green, Emerald green), especially in horticultural work, has developed a manufacturing industry that a few years ago was of small magnitude; its principal use, before 1870, being as a green pigment, with price varying from 30 cents to 40 cents per pound. For this purpose, however, it never ranked as a permanent colour ("Paints, Colours, Oils, and Varnishes," G. H. Hurst, p. 170), and its manufacture was gradually decreasing when its use as an insecticide developed.

In 1896 the manufacture increased to such an extent that the price was reduced to 17 cents per pound, and at the present time is quoted at 12½ cents per pound.

The article as formerly prepared for pigment purposes was of uniform composition, or nearly so; but of late years, either in hurrying the manufacture or by needlessly adding excess of arsenious oxide, the variation in composition is very marked.

Not only is this so of the production by any one manufacturer of his various outputs, but if samples be taken at random in the market it is seldom that two can be found of similar composition. This has led to many complaints by the dealer and by the horticulturist; by the former, that he, with the aid of the chemist, has found the composition not constant; and by the latter, that Paris green fails in many instances as an insecticide, since it is well known that, with certain percentages of arsenious oxide, combined as arsenite therein, the action is nil.

When pure, the composition of Paris green may be stated as an aceto-arsenite of copper—a combination of arsenious acid, oxide of copper, and acetic acid; having CuO 31.29 per cent, As₂O₃ 58.65 per cent, and acetic acid 10.06 per cent ("Report N.J. Agricultural Experiment Station," 1897, p. 408).

This formula is empirical, since a portion of the arsenic may exist as arsenic acid as well as arsenious acid, and copper suboxide may be present in small amounts with the copper oxide.

Adulteration, in the sense of foreign material added, is rare with the manufacturers of Paris green in this country, and I have failed to find recorded any analyses showing contamination with barium sulphate or calcium carbonate.

The following analyses, in 1897, made by Mr. W. S. Myers, Chemist at the State Agricultural College, New Brunswick, N.J. ("Report N.J. Agricultural Experiment Station," 1897, p. 408) will show the variation in the amounts of As₂O₃ in the samples of Paris green submitted to him:—

Manufacturer.	Dealer.	As ₂ O ₃ .
John Lucas and Co.	J. J. Collins and Son	47.82 p.c.
Wetherell and Co.	From manufacturer	64.88 "
Unknown	J. B. Anistaki	56.19 "
Cawley, Clark, and Co.	C. Ribsam and Sons	68.59 "
C. T. Reynolds	Wm. Rust and Sons	58.44 "
Cawley, Clark, and Co.	Freehold Grange	41.54 "
Robert Shoemaker	From manufacturer	56.03 "
John Lucas and Co.	J. J. Collins and Son	63.11 "
Leggett and Bro.	Wm. Rust and Sons	59.33 "

Mr. Myers found no adulteration whatever in any of the samples, but the percentage of As₂O₃ in many was excessive, and as this chemical is cheaper than the other constituents, fraud would be indicated in this direction.

Messrs. Cawley, Clark, and Co., manufacturers, in reply to question of guaranteeing the percentage of arsenite, state:—"We do not make many assays of our green, but we have made several at considerable intervals, and found

the composition approximately constant. We have another check which confirms this, viz., by weighing each batch, and we find from given amounts of materials that yield is sensibly constant. As our green is composed only of arsenious acid, copper oxide, and combined acetic acid, a simple calculation will show you that the cost of production would be lessened by increasing the percentage of arsenic."

Messrs. John Lucas and Co. state:—"The only explanation we could give you for the variation in the amounts of arsenic is found in the well-known fact that most tests or formulæ for products rarely have a definite or absolute proportion assigned—or, in other words, considerable latitude is allowed, unless the product may be one that is little called for. The theoretical combination, as stated by Mr. Smith, is 58.65 per cent, but Paris green is made in large batches of 5, 10, or 20 tons, and at certain seasons of the year the manufacturer is urged to the utmost to turn it out fast enough; hence sufficient time is not given to the process or the variation would not be more than 5 per cent either way as compared with the theory."

John B. Smith, Sc.D., State Entomologist, N.J., comments as follows ("Report Agricultural Experiment Station, N.J.," 1897, p. 411):—

"Though not directly so stated, these gentlemen admit the possibility of a variation as great as 15 per cent in their product, but seem to consider it immaterial from a practical standpoint. In this I must dissent, for a difference of even 10 per cent of arsenic may make all the difference between an effective and ineffective application. From all the facts obtainable it seems certain that Paris green varies in the percentage of arsenic under the best conditions, and that it may be present either as an arsenite or as an arsenate. Manufactured in large quantities, the difficulties in obtaining a satisfactory result increase, so that a difference of 25 per cent may exist in an absolutely unadulterated product. It follows that, as has been practically found by farmers, the material is not reliable and results are not constant."

In reply to a letter from the writer to Prof. Voorhees, Director of the N.J. Agricultural Experimental Stations, regarding adulteration of Paris green, the following communication was received:—

New Jersey Agricultural Experimental Stations,
New Brunswick, N.J., May 11th, 1898.
EDWARD B. VOORHEES, Director.

Dr. THOMAS B. STILLMAN, Hoboken, N.J.

DEAR SIR,—I have your letter of the 10th inst. concerning the adulteration of "Paris green." I have to say in reply, that in our experience, there is a very wide variation in the composition of different samples of "Paris green," but thus far we have been unable to positively detect adulterations. "Paris green" has also been examined for adulteration in Massachusetts and in Alabama, but in neither State have they been able to find any serious adulteration.

Very truly yours,

E. B. VOORHEES.

Paris green* manufactured in Germany is often adulterated with barium sulphate. Post ("Technisch-chemische Analyse," p. 367) mentions the following as added impurities:—Barium sulphate, calcium carbonate, chrome yellow, and iron oxide.

Wagner ("Chemical Technology," p. 458) states:—"Schweinfurt green (Paris green), in Germany, is known under a number of aliases derived from the peculiar depth of hue as modified in various manufactories by means of barium sulphate, lead sulphate, and chrome yellow.

N. Reitter ("Wittsteins Vierteljahrschrift," VII., p. 359) analysed two samples of Paris green ("Schweinfurt grün") of German manufacture, with the following results:—

* Scheele's green is often mistaken for Paris green, since it is also an arsenite of copper; it, however, contains no acetate, its formula being CuAs₂O₃·CuO·2H₂O.

	No. 1. Per cent.	No. 2. Per cent.
Copper oxide (CuO)	29.370	29.181
Arsenious acid (As ₂ O ₃) ..	48.070	46.839
Acetic acid	6.628	10.230
Water	2.500	2.500
Barium sulphate.. ..	13.432	11.250
	100.000	100.000

C. Reinhard ("Wagner's Theorie und Praxis de Gewerbe," Bd. i., p. 489) found in two varieties of Paris green, chromate of lead, and in one sulphate of barium. Thus:—

	No. 1. Per cent.	No. 2. Per cent.
Copper oxide (CuO)	21.77	24.31
Arsenious acid (As ₂ O ₃) ..	40.28	52.42
Acetic acid	6.20	8.86
Chromate of lead	6.56	14.41
Barium sulphate	25.19	—
	100.00	100.00

Dammer ("Handbuch der Chemischen Technologie," 1898, v., p. 556) states that Schweinfurter-grün has several trade names in Germany, depending upon its composition, as follows:—Englischgrün, Patentgrün, Hörmann's grün, Papageigrün, Kaisergrün, Königsgrün, Wienergrün, Kirchnergrün, Leipzigergrün, Zwickauergrün, Baselergrün, Parisergrün, Neuwiedergrün, Würzburgergrün, and Jasnügergrün. Variation in colour is produced by the addition of any of the following substances:—Gypsum, barium sulphate, chromate of lead, zinc yellow, sulphate of lead, calcium carbonate, &c.

The employment of chromate of lead has a special use in the lightening of the colour for use of the pigment in the textile industries, such as in wall-paper, tapestry, &c., but not in its use as an insecticide.

As chromate of lead is much more expensive than arsenious acid, the conclusion reached in regard to adulteration would be that Paris green, manufactured in this country and used in horticultural work, is practically free from adulteration, whereas, if manufactured for use as a colour with various shades of green, it may contain all the substances enumerated above in addition to the constituents requisite for its manufacture.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 2nd, 1899.

Dr. W. H. PERKIN, F.R.S., Vice-President, in the Chair.

MESSRS. F. J. Beale, George Young, H. Royal-Dawson, E. T. Shelbourn, S. J. Peachey, H. A. Thiersch, R. W. Lindsay, S. Dickson, F. N. A. Fleischmann, and C. Simmonds, were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. James William Anderson, 1, Preston Villas, Halling, Kent; Francis Paul Armitage, High House, Brook Green, Hammersmith, W.; Frederick William Armstrong, The Hill, Langport, Somerset; Frederic Arnold Beesley, Bank House, Wirksworth, Derby; Edgar Marsh Chapman, 17, Bloomsbury Square, W.C.; John Arthur Dewhurst, 125, Mount View Road, Stroud Green, N.; Frank Rawlinson Duddridge, 45, Sidney Grove, Newcastle-on-Tyne; Herbert Frederick Francis Burdett Fermor, 15, Ansdell Road, Peckham, S.E.; Elliott Henry Gurney, Albert Street, Marrickville, New South Wales; Henry Wulff Kinnersley, 4, The Avenue, Keynsham, Somerset; William Thomas Leeming, 60, Lomeshaye

Road, Nelson; Stephen Joshua Lett, 25, Percy Street, Liverpool; Edward Watkin Lewis, 64, Ommaney Road, New Cross, S.E.; Wm. D. McCreath, The Plains, Totnes, S. Devon; Harry Ainley Neale, Brentwood, Clothorn Road, Didsbury, Manchester; Thomas Henry Palmer, "Amalfi," Longueville, Sydney, New South Wales; Marchant Pearson, The Grammar School, Bridlington; Bennett C. Polkinghorne, 46, Lynette Avenue, Clapham Common, S.W.; Georges Ponthieu, Pharmacie Centrale de France, Avenue de Paris, St. Denis, Seine; William Downing Raynor, 13, Christ Church Road, Doncaster; Christopher Foulis Roundell, Guards' Club, Pall Mall, S.W.; William Russell, Thetford, Norfolk; Robert Hawks Walton, 424, Park Road, Moore Park, Sydney, N.S.W.; F. R. Leyland Wilson, Charterhouse, Godalming; John Wilson, 73, Melford Road, Leytonstone, E.

The Chairman referred to the great loss the Society had sustained through the deaths of its illustrious former President, Sir Edward Frankland, and its Foreign Member, Professor Bunsen.

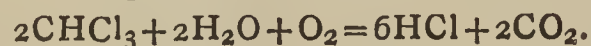
Of the following papers those marked * were read:—

*120. "On Methods for Determining the Relative Proportions of Gaseous Chloroform and Air in a Mixture of the Two, and on a Method for producing a Mixture of Air and Chloroform in any Desired Proportion." By A. VERNON HARCOURT.

To produce anæsthesia, air is inhaled mixed with a small percentage of chloroform vapour. The proportion of chloroform most suitable for this purpose has not been determined, probably for want of a good chemical method of making this determination. The reaction which takes place between chloroform and a hot alcoholic solution of potash, $\text{CHCl}_3 + 4\text{KOH} = 3\text{KCl} + \text{HCO}_2\text{K} + 2\text{H}_2\text{O}$, seemed to furnish a basis for such a method. However, with regard to this reaction, two statements have been made, that all the chlorine of chloroform can thus be converted into a chloride and that it cannot. The author has worked out and described a method for removing chloroform vapour from air, and obtaining chloride from it by means of the above reaction; but on applying the method to weighed quantities of chloroform the results were always about 4 per cent too low. This error is so nearly constant that the method may be used and the results increased by 4 per cent.

A better method depending on a reaction (which, as far as the author knows, is new) has since been worked out by him.

When the mixture of air and chloroform is mixed with a certain proportion of steam by heating it with a few c.c. of water to 50° or 60°, and a platinum wire is kept in a state of incandescence in this mixture, the whole of the chloroform undergoes the following change:—



With a fairly bright wire the change is complete in an hour, and the hydrogen chloride may be obtained in dilute solution by bringing in 20 c.c. of water, and may be determined in the flask with a standard solution of ammonia. If enough steam is not present, or the platinum wire is not heated beyond a low incandescence, or sufficient time is not allowed, a smell of chlorine will be observed at the mouth of the flask and the result will be too low. It was ascertained incidentally that a weighed quantity of chlorine, treated as above, is completely converted into hydrogen chloride. Doubtless the changes—



both occur, but the water present gradually withdraws all hydrogen chloride from the system.

The author also described a method of producing a mixture of air and chloroform in any desired proportion and of constant composition. This consisted in blowing air through a mixture of chloroform and alcohol. The density of the liquid, showing the proportion of its ingredients, could be observed during the passage of the air by

means of two little glass bulbs, of which one floated and one sank when the density was right, and be adjusted by additions of chloroform. Density and temperature being constant, the proportion of chloroform taken up by the air was constant also. To remove alcohol vapour, the current of air was then passed through two wash-bottles containing sulphuric acid and water respectively.

DISCUSSION.

In reply to remarks by Mr. Hehner and Dr. Perkin, Mr. HARCOURT said he doubted whether the use of a Lux balance for observing the density of the gas-stream would be as convenient as the Wolfe's bottle with two floats which he had used. The great difference in density of alcohol and chloroform made the density of the liquid in this case a good index of its composition. He thought a liquid less volatile than alcohol might be found and might have advantages; but alcohol answered well, was innocuous even if a little of its vapour passed on, and could easily be got pure.

*121. "The Theory of Saponification." By J. LEWKOWITSCH.

The author showed that the view of the theory of saponification, according to which the hydrolysis of triglycerides is considered a tetramolecular reaction, must be abandoned in favour of the theory propounded by Geitel, who regards the reaction as bimolecular. If this be so, diglycerides and monoglycerides should occur in partially hydrolysed fats. The author has demonstrated their presence by acetylating the intermediate products, freed from glycerol, and proving that the acetylated products exhibit considerable acetyl values, which rise and fall with the progress of saponification. Additional proof was obtained by determining the amounts of the insoluble fatty acids of the acetylated products, and also their saponification values. The curves illustrating these two series of values correspond to the acetyl curves in a very satisfactory manner.

DISCUSSION.

Dr. LEWKOWITSCH said, in reply to questions from Mr. Blount and Mr. Hehner, that he had not tried any other methods beyond those mentioned, as, in his opinion, they were sufficient to give a satisfactory answer to the point at issue. The proportion of glycerine in the partially saponified samples might have been determined as a further proof, but the methods employed were shorter and more reliable. The saponification had been carried out in a manner corresponding to operations on a large scale, and, since the steam pressure alone causes a very violent boiling and mixing of the mass, there could be little doubt that the samples taken did represent the average. He had not made use of water as a saponifying agent.

*122. "Note on the Action of Dilute Nitric Acid upon Oleic and Elaidic Acids." By F. G. EDMED, B.Sc.

In the course of some experiments on the oxidising action of nitric acid upon oleic acid, the author found that, by using nitric acid of sp. g. 1.2—1.3, the sole action was an isomeric change from oleic to elaidic acid. If the density of the acid did not exceed 1.25 and the action took place in the cold, the yield of the elaidic acid was quantitative. Increase in the strength of the nitric acid and rise of temperature diminished the yield. The rapidity of the change was dependent on the purity of the oleic acid. The dilute nitric acid used in the experiments was carefully freed, by prolonged boiling, from nitrous acid, which is known to bring about a similar change.

Nitric acid of the strengths indicated above has no action in the cold upon elaidic acid itself. Hot concentrated nitric acid decomposes it only upon prolonged boiling.

DISCUSSION.

Mr. EDMED said, in reply to Dr. LEWKOWITSCH, that the specimen of elaidic acid thus prepared melted at 45° C.

*123. "Formation of Tetrazoline." By S. RUHEMANN and H. E. STAPLETON.

On heating monoformylhydrazide at 210—220° for about six hours, the authors obtained a good yield of tetrazoline,—



The hydrochloride of this base, $\text{C}_2\text{H}_4\text{N}_4\cdot\text{HCl}$, had been prepared recently by Pellizzari (*Atti R. Accad. dei Lincei*, 1899, [v], viii., I, 327) by heating diformylhydrazide and treating the crystalline product thus formed with hydrochloric acid. The authors find the melting-point of this salt to be 151—152°. The free base is extremely soluble in alcohol and in chloroform, sparingly so in petroleum-ether. It crystallises from a mixture of chloroform and alcohol in colourless needles which melt at 82—83°, are very deliquescent, and give with copper sulphate a blue colouration. The picrate, $\text{C}_2\text{H}_4\text{N}_4\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$, forms yellow prisms, soluble in alcohol only with great difficulty.

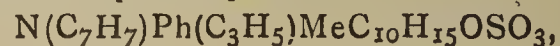
DISCUSSION.

Dr. GEORGE YOUNG said that the authors of this paper had discarded the name dihydrotetrazine in favour of tetrazoline, the term introduced by Pellizzari. This was to be regretted as tending to confusion in the nomenclature of the carbo-nitrogen cyclic compounds. Dihydropyrrole was known as pyrroline, dihydropyrazole as pyrazoline. Tetrazoline should denote dihydrotetrazole, and not dihydrotetrazine. The name isotetrazoline was in use for certain dihydro-derivatives of tetrazole.

Mr. STAPLETON, in reply, said that although the alteration by Pellizzari of the name dihydrotetrazine into tetrazoline was perhaps not altogether satisfactory, it had been accepted both by Pinner and Bamberger, and accordingly the authors of the paper had not hesitated to employ the term.

*124. "Asymmetric Optically Active Nitrogen Compounds. Dextro- and Lævo-benzylphenylallylmethylammonium Iodides and Bromides." By WILLIAM JACKSON POPE and STANLEY JOHN PEACHEY.

On heating the α benzylphenylallylmethylammonium iodide prepared by Wedekind (*Ber.*, 1899, xxxii., 517) with one molecular proportion of silver dextrocamphorsulphonate dissolved in acetone and ethyl acetate, filtering, and evaporating to dryness, a crystalline residue was obtained which by fractional crystallisation from solution in acetone and ethyl acetate, may be resolved into the less soluble constituent, *dextro- α -benzylphenylallylmethylammonium dextrocamphorsulphonate*,—



and the more soluble isomeric dextrocamphorsulphonate of the *lævo-base*; the former has the molecular rotation in aqueous solution $[\text{M}]_{\text{D}} = +208^\circ$, and the latter $[\text{M}]_{\text{D}} = -87^\circ$.

On adding potassium iodide or bromide to aqueous solutions of these salts, the corresponding iodide or bromide is precipitated, and may be purified by crystallisation from alcohol; the following salts were thus obtained:—*Dextro- α -benzylphenylallylmethylammonium iodide*, $\text{N}(\text{C}_7\text{H}_7)\text{Ph}(\text{C}_3\text{H}_5)\text{MeI}$ $[\alpha]_{\text{D}} = +52.4^\circ$. *Dextro- α -benzylphenylallylmethylammonium bromide*,—



Lævo- α -benzylphenylallylmethylammonium iodide, $[\alpha]_{\text{D}} = -51.4^\circ$. *Lævo- α -benzylphenylallylmethylammonium bromide*, $[\alpha]_{\text{D}} = -67.3^\circ$.

The isolation of these compounds proves that dissolved substances may owe their optical activity to the asymmetry of nitrogen.

It is further shown that Wedekind's iodide is not a racemic compound, but merely an ordinary or pseudo-racemic mixture of the dextro- and lævo-components.

DISCUSSION.

Dr. ARMSTRONG thought this communication was the

most valuable contribution made to stereochemistry since the introduction of geometrical considerations by Le Bel and van 't Hoff.

The discovery of a method of preparing asymmetric nitrogen compounds was not only of intrinsic importance, but afforded a means of investigating the problem which chemists had so long disputed as to the valency of nitrogen in ammonium compounds. It would perhaps be possible, by varying the number of radicles, to discriminate between compounds containing pentad and "molecular" compounds containing triad nitrogen.

Dr. LEWKOWITSCH said he fully appreciated the difficulties attendant on work of this kind, as some time ago he had attempted to prepare silicon compounds possessing optical activity, but so far without success. He ventured to suggest that these experiments might now be resumed.

125. "*Camphoroxime. Part III. Behaviour of Camphoroxime towards Potassium Hypobromite.*" By M. O. FORSTER, Ph.D., D.Sc.

With the object of preparing brominated derivatives of camphoroxime, the author has studied the behaviour of this substance towards alkaline hypobromite.

The compound, $C_{10}H_{16}BrNO_2$, obtained by the action of a concentrated ice-cold solution of potassium hypobromite on camphoroxime, crystallises from alcohol in snow-white, fern-like aggregates, and melts at 220° to a colourless liquid which immediately decomposes; it gives Liebermann's reaction for nitroso-derivatives, and yields camphoroxime on reduction with zinc dust and acetic acid. A 2 per cent solution in benzene gave $[\alpha]_D = -65.6^\circ$.

The compound, $C_{10}H_{14}BrNO$, produced when the foregoing substance is dissolved in concentrated sulphuric acid, crystallises from alcohol in lustrous transparent prisms; it shrinks and darkens at about 210° , becoming completely charred at 220° . This derivative is optically inactive, and does not give Liebermann's reaction. Treatment with hot concentrated hydrochloric acid converts it into an *isomeride*, which separates from alcohol in large transparent six-sided crystals, and melts to a colourless liquid at 240° ; this modification is likewise optically inactive, and does not give Liebermann's reaction; it yields a *benzoyl* derivative, which crystallises from alcohol in lustrous scales melting at $174-176^\circ$.

The *nitrile*, $C_9H_{13}N$, obtained when either of the compounds, $C_{10}H_{14}BrNO$, is heated with aqueous soda, forms a limpid, fragrant oil which boils at $198-199^\circ$ under 760 m.m. pressure, and has sp. gr. 0.9038 at 24° ; it is oxidised by an ice-cold solution of potassium permanganate, and instantly decolourises a solution of bromine in chloroform.

The *amide*, $C_9H_{15}NO$, occurs as a by-product in the preparation of the nitrile, and is formed when that substance is heated with alcoholic potash; it crystallises from light petroleum in white, highly lustrous needles melting at 90° . When this compound is heated with hydrochloric acid, isolauronamide and isolauronic acid are produced, and as campholytic acid is converted by mineral acids into isolauronic acid, it appears probable that the new amide is the hitherto unknown amide of campholytic acid. Experiments are being conducted with the view of ascertaining if this is so.

126. "*Optical Influence of an Unsaturated Linkage on certain Derivatives of Bornylamine.*" By M. O. FORSTER.

Condensation products of bornylamine with aromatic aldehydes have been prepared in order to compare the optical activity of such compounds with the corresponding derivatives of benzylbornylamine.

It is found that transition from benzylbornylamine and its nitro-derivatives to the corresponding benzylidene compounds is attended by a fall in the rotatory power of the benzene and alcoholic solutions; the decrease in the case of the paranitro-derivatives approximates to the rotational difference between benzylbornylamine and benzylidene bornylamine, but is widely divergent from this in the case of the orthonitro-compounds.

Benzylidenebornylamine, o-nitrobenzylidenebornylamine, p-nitrobenzylidenebornylamine, o-hydroxybenzylidenebornylamine, and p-hydroxybenzylidenebornylamine are described in the paper.

127. "*The Interaction of Sodium Hydroxide and Benzaldehyde.*" By CHARLES A. KOHN, B.Sc., Ph.D., and W. TRANTOM, B.Sc., Ph.D.

The object of the investigation was to ascertain if an intermediate compound was formed in the preparation of benzyl alcohol from benzaldehyde and soda. The authors state that, in presence of water, the sole products of the reaction are benzyl alcohol and sodium benzoate. By employing carefully dried materials, however, benzyl benzoate is formed to the extent of 10 per cent. The reactions which occur are explained by the following equations:—

1. $2C_6H_5 \cdot CHO + NaOH = C_6H_5 \cdot C(ONa)(OH)(OC_7H_7)$.
2. $C_6H_5 \cdot C(ONa)(OH)(OC_7H_7) = C_6H_5CO_2Na + C_7H_7OH$.
3. $C_6H_5 \cdot C(ONa)(OH)(OC_7H_7) = C_6H_5CO_2C_7H_7 + NaOH$.

Reaction 2 is favoured by the presence of water and excess of soda; reaction 3 by an excess of aldehyde.

128. "*Electrolytic Preparation of Induline Dyes.*" By E. C. SZARVASY, Ph.D.

When a mixture of aniline hydrochloride and aniline is fused and electrolysed under given conditions, induline colouring matters are formed. The author describes the apparatus he constructed to carry out these experiments. The following products were separated:—

Induline, $C_{18}H_{13}N_3$; B₄, anilidoinduline, $C_{24}H_{18}N_4$; induline 6B, $C_{30}H_{23}N_5$; and azophenine, $C_{36}H_{29}N_5$.

The results prove (1) that the chlorine produced by the electrolytic decomposition of the aniline hydrochloride effects diazotisation, (2) that under certain conditions the azo-compounds thus formed react with the hydrochloride of aniline, forming (3) primarily azophenine, (4) ultimately indulines.

129. "*The Heat of Combination of Copper with Zinc.*" By T. J. BAKER, B.Sc.

The only work in this direction hitherto appears to be by Dr. Galt (*Rep. Brit. Ass.*, 1898, and *Proc. Roy. Soc. Edin.*, 1899) and by Herschkowitsch (*Zeit. f. Phys. Chem.*, 1898, xxvii., 123). Neither appeared until this work was nearly completed, and in each case the number of observations appears to have been small. In the present research the method consisted in the determination of the difference between the heat of solution of an alloy of the two metals and that of an equal weight of a mixture in the same proportions. Actual determinations of the latter quantity were made, as it was not found possible to calculate it exactly from the heat of solution of the separate metals.

Two solvents were used. (a) Chlorine water—0.15 normal. (b) $HNO_3 \cdot 3H_2O$.

Only alloys with less than 42 per cent copper could be so finely powdered as to dissolve quickly in chlorine water. With nitric acid as solvent, a series of twenty-one alloys—all made from the purest metals obtainable and carefully analysed—was examined. The results obtained by both methods agree very well.

The results are expressed in the form of a curve with percentages of copper as abscissæ and heats of formation of 1 grm. of alloy as ordinates. From 0 to 30 per cent of copper no heat of combination could be detected. This renders doubtful the existence of the supposed compound, $CuZn_2$ (Laurie, Charpy, and Herschkowitsch).

From 30 to 62 per cent of copper, the curve rises to an ill-defined maximum of 46 calories per grm. of alloy. This alloy (62 per cent copper) does not correspond to any simple atomic compound, but is otherwise remarkable (see 4th Report of the Alloys Research Committee, Institution of Mechanical Engineers).

From 62 per cent copper onwards, the curve gradually sinks to zero at 100 per cent copper.

Hence copper and zinc evolve heat when alloying with

one another, a point of interest with reference to the electro-deposition of brass.

The bearing of these experiments on Lord Kelvin's estimate of the limits of molecular dimensions is briefly discussed.

130. "*The Action of Sulphuric Acid on Fenchone.*" By J. E. MARSH.

The author shows that by the action of strong sulphuric acid on fenchone, aceto-xylene (Me: Me: Ac=1:2:4) was produced in quantity approximating to the total amount required by theory, and considers this fact to be opposed to the constitution of fenchone recently put forward by Wallach and by Gardner and Cockburn.

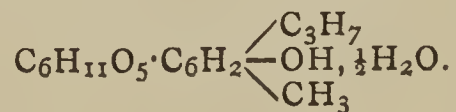
131. "*On Glucosides.*" By HUGH RYAN, M.A.

By the action of acetochloroglucose on solutions of phenols in alcoholic potash, crystalline glucosides of the β series were obtained.

$\beta\beta$ -Naphthol-glucoside, $C_6H_{11}O_5 \cdot OC_{10}H_7$, prepared from acetochloroglucose and β -naphthol, crystallises in long needles [m. p. $184-186^\circ$], is easily soluble in alcohol and in hot water, difficultly soluble in acetone, and scarcely soluble in benzene, ligroin, cold water, or ether, is readily hydrolysed either by dilute acids or emulsin, reduces Fehling's solution only after hydrolysis, is stable towards dilute alkali in which it is insoluble, and has a disagreeable taste.

β -*p*-Cresol-glucoside m. p. $175-177^\circ$, and β -*o*-cresol-glucoside, $C_6H_{11}O_5 \cdot OC_6H_4CH_3$, m. p. $163-165^\circ$, resemble one another as well as naphthol-glucoside, crystallising from water in needles which are scarcely soluble in ether, benzene, or ligroin, but are fairly soluble in alcohol and in water, do not reduce Fehling's solution, are readily hydrolysed and possess a bitter taste.

β -Carvacrol-glucoside, m. p. 135° , crystallises from water in needles not readily soluble in ether or cold water, easily soluble in alcohol and in acetone, but scarcely soluble in benzene, chloroform, or ligroin. It does not refuse Fehling's solution, dissolves slowly in dilute alkali, and is hydrolysable by means of dilute acids or emulsin. Its formula is either $C_6H_{11}O_5 \cdot OC_6H_3 \cdot C_3H_7 \cdot CH_3 \cdot \frac{1}{2}H_2O$, or



d-Pentacetyl-glucose (m. p. 110°) is obtained by the action of 20 mols. of acetyl chloride on 1 mol. dry glucose in an open vessel.

Acetochloro galactose, a colourless semi-solid mass, was got by the action of acetyl chloride on galactose in a closed tube, and has been converted into a galactoside of β -naphthol.

(To be continued).

CORRESPONDENCE.

THE ACTION OF WATER ON MAGNESIUM.

To the Editor of the Chemical News.

SIR,—I can fully endorse one of the conclusions arrived at by Mr. Bryant in his communication published in the CHEM. NEWS of November 3rd (vol. lxxx., p. 183), for I have regularly demonstrated the production of hydrogen from water by magnesium at ordinary temperatures for the past four years, and was under the impression the fact was well known.

The junior students here, when studying the action of water on metals, by allowing them to stand in contact for a week, notice bubbles of a gas on magnesium ribbon when it is used. Later on, when they have discovered that hydrogen exists in water, their attention is directed back to the appearance of the bubbles, and the gas is collected and identified in the following way:—

About a yard of clean magnesium ribbon is loosely screwed up and placed in a four-ounce flask fitted with cork and narrow delivery tube. The flask is filled with cold water and the cork replaced, so that the whole tube is filled with water. On standing 24 hours sufficient gas may be collected to identify it.

One peculiarity about the gas so generated is that it burns with a peculiar greenish flame. Is it not possible that traces of a hydride may also be formed? This is at present under investigation.—I am, &c.,

WILLIAM FRENCH.

Bury Grammar School,
Nov. 11, 1899.

LABORATORY LAMP.

To the Editor of the Chemical News.

SIR,—I should be grateful to any of your readers who can suggest a good lamp, to do the work of an ordinary Bunsen burner, for use in a country laboratory where gas is not obtainable.—I am, &c.,

CHEMICUS.

November 18, 1899.

NOTICES OF BOOKS.

Determination of Radicles in Carbon Compounds. By H. MEYER. Authorised Translation, by J. BISHOP TINGLE. New York: John Wiley and Sons. London: Chapman and Hall, Lim. 1899. Pp. x.—133. 12 mo. Ill.

DR. TINGLE'S translation of Dr. Meyer's well-known book seems to be very carefully done, and will be welcomed by those instructors wishing to use it with classes in England and America. The work deals with quantitative work in organic chemistry, and is adapted for advanced students. Chapter I. deals with the determination of hydroxyl by acylation, by alkylation, by the preparation of carbamates, and by the formation of esters of phenylcarbamic acid. In Chapter II. the determination of carboxyl is treated in several ways:—A. Analysis of metallic salts of the acid. B. Titration. C. Etherification. D. Determination of the electrolytic conductivity of the sodium salts. E. Indirect methods, such as the carbonate, ammonia, hydrogen sulphide, and the iodine methods.

A valuable feature are the numerous references to literature. A few woodcuts are introduced to elucidate the subject. An Index of Authors, and a separately alphabetized Index of Subjects close the volume. The advantage of printing the indexes separately, in two alphabets, is not evident to the reviewer.

The book fills a place occupied by no other.

H. C. B.

The Manufacture of Carbons for Electric Lighting and other Purposes: a Practical Handbook. By FRANCIS JEHL, Member of the American Institute of Electrical Engineers. London: The Electrician Printing and Publishing Company. Pp. 232.

THE manufacture of carbons for electric lighting purposes is a business which has made very rapid strides within a comparatively short period of time, not only as regards quantity, but also in quality. It is rare indeed at the present day to see arc lamps giving a violet light, due to the presence of potash salts in the carbons. Ten or fifteen years ago such a thing was the rule rather than the exception.

We have in this volume a complete description of the art of making carbons, electrodes, &c., the various gas generators and furnaces used in carbonising, with a plan for a model factory.

The author points out that the literature on this subject

is very limited. We are of opinion that this is to be accounted for by the fact that most makers have trade secrets of great value to themselves, which they are unwilling to give to the world; for this we cannot blame them.

The book is well printed, and contains a great deal of interesting and important information on the subject.

The Rise and Development of the Liquefaction of Gases.

By WILLETT L. HARDIN, Ph.D. New York: The Macmillan Company. 1899. Pp. 250.

ALTHOUGH the literature on this subject may be somewhat scattered, as stated by the author of this work, consisting to a great extent of notices in various technical journals, we may reasonably claim that every success which has been obtained by the few accredited workers in this domain of scientific research has been promptly notified to the readers of the CHEMICAL NEWS.

The name of Dewar stands out pre-eminently as that of the man who has imagined and carried out some of the boldest and most remarkable experiments in this branch of physical and chemical investigation; and, having recently succeeded in solidifying hydrogen, he may echo Alexander's lament that there are no more worlds to conquer.

The development of the methods used in this particular line of research has been accompanied by much disappointment and failure, and although liquid oxygen can now be produced at a comparatively low price, it must be remembered that the first ounce made cost many hundreds of pounds.

The author divides the progress of this work into four periods: the first being mostly historical, and not of much practical importance; the second begins with the work of Faraday, during whose time the methods of producing high pressures and low temperature were greatly developed; the third deals with critical constants, and the continuity of the gaseous and liquid states of matter; while the fourth begins with an account of the experiments of Messrs. Pictet and Cailletet in the year 1877 and extends to the present time. This last period, which only embraces a little more than twenty years, is by far the most fruitful in results; the value of which may be understood when we point out that more than one-half of this volume is devoted to this period alone.

The author has, we believe, produced the first systematic work on this subject, and deserves the thanks of the scientific world for his labour.

Edinburgh University Chemical Society.—The President delivered an address on Nov. 6th, his subject being "Bunsen." Prof. Crum Brown sketched the life of Bunsen, and gave an outline of his work, in particular the investigations of cacodyl and its compounds and the elucidation of their constitution; the invention and development of numerous analytical processes and apparatus, including the introduction of scientific and exact methods of gas analysis, of spectrum analysis, and flame reactions; the discovery of caesium and rubidium. He gave some personal recollections of Bunsen and testified to the esteem and love with which he was universally regarded by his pupils.

Filtering Device.—Sargent and Faust (*J. Am. Chem. Soc.* xxi.). For some precipitates, as MnO_2 , phosphomolybdate, &c., a filter made of sand placed in a carbon filtering tube, and covered with a thin layer of asbestos, has been found very satisfactory. A small plug of glass wool is used below to retain the sand in place, and the filter should be washed three or four times with HNO_3 before using.—*School of Mines Quarterly*, xx., No. 4, p. 399.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 18, October 30, 1899.

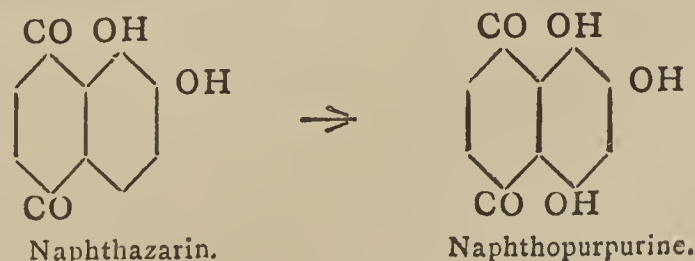
Atomic Weight of Boron.—Henri Gautier.—The author has made four series of determinations of the atomic weight of boron, which give the following numbers:—

	At. weight.	Probable error.
Using boron sulphide	11.041	± 0.017
" carbon boride	10.997	± 0.017
" boron bromide	11.021	± 0.006
" boron chloride	11.011	± 0.008

The determinations carried out on boron sulphide and carbon boride, compounds very different from one another, tend to show that the atomic weight of boron is very near to 11. But in spite of the advantages resulting from their small molecular weight, these two substances are more difficult to obtain pure than the chloride and bromide. The mean of the values given above is 11.016, and is the one the author proposes to adopt. It is very near to 11 and a little greater than those previously found by Abrahall and again by Ramsay and Aston.

Mixed Anhydrides of Acyclic and Cyclic Acids.—A. Béhal.—The author has studied particularly the mixed aceto-isovaleric and acetobenzoic anhydrides. In the first case, preparing aceto-isovaleric anhydride by the methods of Gerhardt or Autenrieth, the products obtained in the two cases do not give a constant composition. The presence, therefore, of this anhydride can only be explained in three ways:—(1) The product formed is a mixture of acetic anhydride and isovaleric anhydride, and the first is more rapidly destroyed than the second by the alkaline solution. (2) The product is the mixed anhydride, and under the influence of the reagent is transformed into the alkaline acetate and isovaleric anhydride. (3) The product is a mixture of the mixed anhydride and isovaleric anhydride. The first is more easily destroyed than the second by the conditions under which it is prepared.

Naphthopurpurine, an Oxidation Product of Naphthazarine.—George F. Jaubert.—Whilst examining the action of nitric acid on Roussin's naphthazarine the author remarked that, under certain conditions, a red colouring matter is formed. An estimation of the nitrogen present showed that it was not a nitrogen derivative, but a simple product of oxidation.



Sublimed naphthopurpurine is in the form of reddish brown needles, which easily melt on a strip of platinum, giving off red fumes smelling of quinone. It is not easily soluble in cold water, but very easily in hot water, from which it crystallises in tufts on cooling. It is very soluble in alcohol and acetic acid, giving a red solution. Naphthopurpurine is a trioxy- α -naphthoquinone, analysis giving—

C	58.42
H	3.05

Calculating for the formula $C_{10}H_6O_5$ the results are—

C	58.25
H	2.92

MEETINGS FOR THE WEEK.

MONDAY, 27th.—Society of Arts, 8. (Cantor Lectures). "Enamelling upon Metals," by Henry Hardinge Cunynghame.
WEDNESDAY, 29th.—Society of Arts, 8. "The Great Seals of England," by Allan Wyon.

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All persons desiring to be admitted as Workers must send evidence of scientific training, qualification, and previous experience in original research, along with a statement of the nature of the investigation they propose to undertake.

MICHAELMAS TERM.—Monday, October 2, to Saturday, December 16.

LENT TERM.—Monday, January 8, to Saturday, April 7.

EASTER TERM.—Monday, April 30, to Saturday, July 28.

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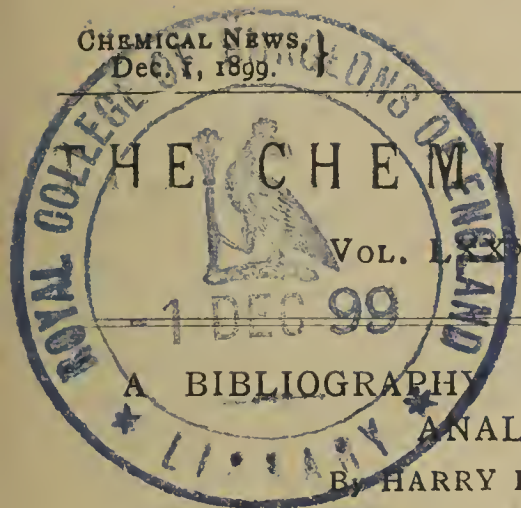
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CHEMICAL NEWS.

VOL. LXX., No. 2088.

A BIBLIOGRAPHY OF STEEL-WORKS ANALYSIS.

By HARRY BREARLEY.

(Continued from p. 246).

MANGANESE (continued).

IV. VOLUMETRIC ESTIMATION OF MANGANESE.

a. Titrations with Standard Permanganate.—

87. GUYARD (C. N., viii., 292).—Titration at 80° C. Associated metals are converted to peroxides, and do not interfere. The process separates Mn from alkalis, Ca, Sr, Mg, Ni, Co, Zn, and Ur. (Some of the separations are not nearly exact ones.—H. B.). Discusses three permanganates of MnO : — $5\text{MnO} \cdot \text{Mn}_2\text{O}_7$, $4\text{MnO} \cdot \text{Mn}_2\text{O}_7$, and $3\text{MnO} \cdot \text{Mn}_2\text{O}_7$.
88. HABICH (C. N., xii., 58).—Dilute H_2SO_4 and HCl; lower oxides of Ni and Co, ZnO, Al_2O_3 , and CaO do not interfere with Guyard's process. Strong HCl or H_2SO_4 , Fe_2O_3 , and Cr_2O_3 render the process useless.
89. GORGEU (J. I. S. I., 1894, i., 613).—Results by Guyard's process too low, partly on account of the acidity of the liquid. Donath's modification (see 100) also gives inexact results unless the solutions are slowly mixed. Criticises Guyard's views (see 87) concerning existence and constitution of the compounds formed during the titration.
90. VOLHARD (C. N., xl., 207).—Manganous solution mixed with ZnSO_4 , made faintly acid with HNO_3 , and titrated near boiling-point to a permanent red colour.
91. AUCHY (C. N., lxxiv., 214).—Examination of Volhard's process for estimation of Mn in steels. Add ZnO to cold solution until Fe is precipitated, then excess of ZnO; titrate at boiling-point, and deduct 0.02 per cent.
92. HASWELL (J. I. S. I., 1882, 743).—Acidification with a few drops of HNO_3 previous to titration counteracts traces of organic matter. Standardise permanganate with KI and thiosulphate.
93. DAW (C. N., lxxix., 25).—Titrations with permanganate are subject to error on account of organic matter, reckless addition of ZnO, and standardising solutions with Fe instead of Mn. Process described to eliminate these errors.
BREARLEY (C. N., lxxix., 47) takes exception to permanganate being standardised by the Mn_3O_4 finally heated over a blast-lamp. The validity of this procedure is discussed (pages 58, 83, and 104).
94. WOLFF (J. I. S. I., 1885, 301).—Separates Fe with ZnO; no filtration; excess ZnO to be avoided; KClO_3 used to oxidise Fe; HNO_3 leads to organic compounds, which interfere with titration. Results slightly low.
95. SARNSTROM (C. N., xlvii., 177).—Sodium bicarbonate added in small quantities until Fe is precipitated; titration by Guyard's process without filtering off the Fe.
96. AUCHY (J. C. S., lxxii., ii., 603).—The danger of Mn being carried down by the precipitated ferric oxide greatly lessened if about 7 grms. $(\text{NH}_4)\text{Cl}$ is added before the sodium carbonate in Sarnstrom's process.
97. MIXER and DUBOIS (C. N., lxxv., 51).—A study of Sarnstrom's method. Add Fe_2Cl_6 if Fe is low; use large amounts HCl, so as to generate CO_2 ; large excess carbonate to be avoided. Not reliable for high percentages.

98. BREARLEY (C. N., lxxv., 13).—Acetate separation of Fe; faintly acid filtrate poured into excess of permanganate mixed with ZnSO_4 (Wright and Meinecke's modification of Guyard's process, see J. C. S. Trans., 1880), and excess permanganate titrated; or the precipitated MnO_2 may be estimated. Excessive ammonia salts to be avoided (see 109). Describes syphon filter and general corrections for hot aliquot filtrations.
99. SCHÖFFEL and DONATH (J. C. S., lii., 399).—Neutralised with sodium carbonate; add to permanganate and ZnSO_4 ; excess titrated with arsenious acid.
100. DONATH (C. N., xliii., 253; and SCHÖFFEL and DONATH, J. I. S. I., 1883, 381).—Neutral solution of Mn salt flows into hot alkaline permanganate; process ended when supernatant liquid is colourless; Fe present as per-salt does not interfere. Similar process for estimating Cr in presence of Fe and Al.
101. SCHÖFFEL and DONATH (J. I. S. I., 1887, i., 469).—Fe separated with ZnO; without filtration, run into boiling $\text{KMnO}_4 + \text{ZnSO}_4$ —this to avoid formation of lower oxides than MnO_2 . Excess permanganate determined with arsenious acid.
102. GIORGIS (J. I. S. I., 1897, ii., 498; and J. C. S., lxxii., ii., 350).—Neutralised solution of Fe and Mn boiled with permanganate and large amounts of soda nitrate; excess permanganate determined. Similar process for Cr if Mn is absent or present in known amount.
103. GHILIAN (C. N., lix., 121).—Titration in presence of ZnO without filtering off Fe. Twenty-five assays in half an hour.
104. BRAND (J. I. S. I., 1887, ii., 368; and 1888, i., 375; REIS, J. C. S., lxiv., ii., 304).—Sample dissolved in nitro-sulphuric acid, oxidised with HNO_3 and barium peroxide, H_2O_2 boiled off, Fe precipitated with ZnO, and solution titrated; precipitate settles rapidly; continuous working with two burettes.
105. RUBRICIUS (J. I. S. I., 1892, ii., 512).—Precipitates Fe with ZnO, and adds MgSO_4 previous to titration.
106. JOLLES (J. C. S., lvi., 798).—MnO solution added to faintly alkaline solution of standard manganate until it is decolourised; the precipitate is MnO_2 .

Standard Solutions and General Notes.—

107. DUNN (C. N., xlv., 137).—Mixed solutions of MnSO_4 and KMnO_4 evolve little or no gas in the cold; on heating, O is evolved if the permanganate is in excess.
108. MORSE and REESE (C. N., lxxviii., 77).—Permanganate is reduced and O evolved if MnO_2 is present. To this cause is ascribed the instability of KMnO_4 solutions; they should always be carefully filtered.
109. TAMM (C. N., xxv., 26).—Permanganate as an oxidising agent can convert ammonia into HNO_3 .
110. MEYER and RECKLINGHAUSEN (J. C. S., lxxii., ii., 19).—H and CO are slowly oxidised by a solution of KMnO_4 .
111. HARCOURT (C. N., xliii., 293).—Speed of the reaction between permanganate and oxalic acid depends on the relation between permanganate, oxalic acid, manganous sulphate, and sulphuric acid.
112. DYMOND and HUGHES (J. C. S., lxxi., 314).—On titrating H_2SO_3 with KMnO_4 , only 89 per cent of that required to form H_2SO_4 is used; due to formation of dithionic acid. Same amount formed under varying conditions.
113. LONGI and CAMILLA (J. C. S., lxxii., ii., 387).— MnO_2 adhering to vessel during precipitation due to dirt, and may be prevented by washing with $\text{H}_2\text{SO}_4 + \text{CrO}_3$. Ni, CrO_3 , Co, Pb do not interfere with permanganate titration of MnO.
114. LUNGE (J. C. S., xlvi., ii., 62; also J. C. S., lviii., 1469).—Permanganate standardised in acid solution with H_2O_2 ; evolved O measured. A similar pro-

- cess serves to determine available oxygen in pyrolusite, Weldon mud, &c.
115. MORSE and CHAMBERS (*J. C. S.*, lxx., ii., 388).—In presence of a neutral reducing agent, such as H_2O_2 , permanganate may be standardised with H_2SO_4 , or conversely.
116. RIEGLER (*J. C. S.*, lxx., ii., 676).—Solution of oxalic acid containing large amount of H_2SO_4 keeps unchanged for a year.
117. LENZ (*J. C. S.*, xlviii., 598).—Ten grms. boric acid per litre prevents the decomposition of oxalic acid.
118. HAMPE (*C. N.*, xlvii., 260).—Pure dehydrated oxalic acid is obtained by sublimation, and kept over H_2SO_4 .
119. MCDIRBY (*C. N.*, xxx., 142).—Permanganate standardised by simply dissolving piano-wire is inaccurate. The small amount of C existing in the Fe is oxidised also, and errors of 1 to 2 per cent are caused. Berthelot has previously drawn attention to this point.
- IV.b. *Oxidations to Permanganate.*—
120. GIBBS (*C. N.*, xi., 147).—Has recommended boiling with PbO_2 to separate Mn from alkaline earths. A compound, $\text{MnO}_2 + 4\text{PbO}_2$, is formed. [This appears to be the source of error, more or less evident, whenever more than about 0.01 grm. of Mn is boiled in an acid solution with PbO_2 .—H. B.].
121. MORSE (*J. C. S.*, lxxii., ii., 145).—In presence of HNO_3 the following reaction occurs:— $2\text{HMnO}_4 + 3\text{PbO}_2 = \text{H}_2\text{O} + 2\text{MnO}_2 + 3\text{PbO} + 3\text{O}_2$.
122. LECLERC (*C. N.*, xxvi., 297) and PICHARD (*C. N.*, lxxvii., 108).—Oxidises an acid solution of soils, &c., with red lead; it is necessary to destroy organic matter. Not possible to titrate with FeSO_4 on account of PbSO_4 (see 136), or oxalic acid on account of PbCO_3 (see 134). Titrates with HgNO_3 , liquid to be freely acid so as to prevent precipitation of Mn oxides (Guyard's reaction).
123. PECHARD (*C. N.*, xxvii., 85).—Effects solution by fusing with sodium carbonate. Compares with standard permanganate to 1/10,000 by diluting largely.
124. DESHAY (*C. N.*, xxxviii., 70).—Nitric or nitro-sulphuric acid solution of the sample; oxidises with PbO_2 . Always the colouration is stronger as the amount of Mn increases. [This is not true when several centigrms. or more Mn is present.—H. B.]. Tone varies according to origin and degree of oxidation. Essential to operate under like conditions. Titrates with soda arsenite.
125. PETERS (*C. N.*, xxxiii., 35).—Dissolve in HNO_3 ; oxidises with PbO_2 . Finds 1 per cent to be the limit, using 0.1 grm. of the sample. For spiegels, works on 0.004 grm. Combined carbon does not interfere.
126. CHATARD (*C. N.*, xxiv., 196).—Used for dolomite and limestones. Fails for large amounts of Mn. Longer the mixture is boiled more permanganate is there formed, but no limit attainable.
127. MORGAN (*C. N.*, lvi., 82).—Oxidation with PbO_2 . Colour comparison. Estimates Mn in the sample which has served for colorimetric estimation of carbon.
128. SCHLAGDENHAUFFEN (*J. C. S.*, xlviii., 442).—Oxidation with PbO_2 . Concentration of solution not less than 0.1 per cent Mn or 2 per cent HNO_3 . Titrate in very acid solution.
129. HUNT (*J. I. S. I.*, 1886, 1020).— HNO_3 used should be free from Cl or nitrous fumes, and throughout the process should be 1.20 sp. gr.; heats in CaCl_2 bath; compares colours. CHEEVER (*ibid.*) considers the method unreliable.
130. OSMOND (*J. I. S. I.*, 1885, 275).—Dissolve in HCl , evaporate; dissolve in HNO_3 , add soda metaphosphate and PbO_2 . Filtrate compared with standard.
- The error is 1/50th. PbO_2 may be replaced by current of ozonised oxygen.
131. ROSSI (*J. I. S. I.*, 1891, i., 438; and 1892, i., 491).—Like Osmond, but CaCO_3 instead of PbO_2 . When Cl is evolved the solution is filtered and compared with standard.
132. MOORE (*C. N.*, lxiii., 66).—The Mn is oxidised to manganic metaphosphate by means of phosphoric acid and chlorate. The violet liquid is titrated with FeSO_4 and KMnO_4 . Cr is the only metal that interferes.*
134. THORPE and HAMBLY (*J. C. S.*, liii., 182).—Oxidation with PbO_2 in nitro-sulphuric solution, and titrate with ammonium oxalate. Not more than 0.01 grm. Mn should be present.
135. BABBIT (*J. I. S. I.*, 1887, ii., 369).—Oxidation with PbO_2 ; supernatant liquid decanted through asbestos, and residue boiled with 20 per cent HNO_3 so long as the decanted liquid is coloured.
136. WEISMANN (*J. I. S. I.*, 1888, i., 377).—Solution in nitro-sulphuric acid, oxidised with PbO_2 , and titrated with FeSO_4 .
137. SCHNEIDER (*J. I. S. I.*, 1892, ii., 512).—As Weismann; titrated with FeSO_4 and KMnO_4 , Cr and Mn may be thus estimated together. Two grms. of sample used.
138. SCHNEIDER (*J. C. S.*, lxxiv., ii., 94).—Titration of the permanganate solution with H_2O_2 .
139. SCHNEIDER (*J. C. S.*, liv., 873).—Bismuth tetroxide in HNO_3 solution converts Mn to permanganate. Titrate with H_2O_2 ; Fe or H_2SO_4 have no influence.
140. REDDROP and RAMAGE (*J. C. S.*, lxvii., 268).—A modification of the previous process in which sodium bismuthate is used instead of the tetroxide. Permanganate filtered into excess H_2O_2 in HNO_3 , and titrated back with KMnO_4 . Cu and Ni are without effect. Cr and Co = 5 per cent cause only slightly high results. Available for any amount of Mn, and completed in fifteen minutes.
141. VAN GRUNDY (*J. I. S. I.*, 1892, ii., 512).—Oxidation with PbO_2 , and titration with arsenious acid. Method spoken of as Textors.
142. KONINCK (*C. N.*, lix., 230).—Commercial PbO_2 prepared by treating alkaline lead solutions with Cl; this gas carries MnCl_2 derived from its preparation. Hence the presence of Mn in PbO_2 . (Mn-free red lead easy to obtain.—H. B.).

(To be continued).

ON CITRONELLALIDENECYANACETIC ACID.

By F. TIEMANN.

As the author has already shown (*Berichte*, vol. xxxi., p. 3329), the transformation of citral into citronellalidenecyanacetic acid, fusible at 122° , serves as an excellent means for identifying and estimating this aldehyde. As the essential oils often contain citronellal as well as citral, it became interesting to examine how citronellal behaved in the presence of cyanacetic acid.

Five grms. of citronellal were well shaken up with a solution of 2.75 grms. of cyanacetic acid and 2 grms. of caustic soda in 20 c.c. of water. It is best to cool the mixture so as to avoid the formation of accessory resinous products. The alkaline solution is exhausted with ether to eliminate all impurities, acidulated, and again exhausted with ether. By evaporating the ether a residue is obtained, which, after a certain time, takes the form of a crystalline mass which can be dried on a porous plate. The return of citronellalidenecyanacetic acid reaches

* This and Nos. 130 and 131 are not oxidations to permanganate; they are classed here, however, because the operations are very similar.

about 40 per cent of the weight of citronellal used. This acid is insoluble in water, easily soluble in alcohol and ether, and crystallises in alcohol or benzene in tablets, fusible at 137—138°. The sodic salt of this acid is specially characteristic; it is relatively very slightly soluble, and separates out in crystals when citronellalidenecyanacetic acid is dissolved, warm, in a not too weak solution of soda, and then allowed to cool. The sodic salt of citralidenecyanacetic acid remains in solution under the same conditions, but the two acids in solution, neutralised with ammonia, are precipitated by chloride of calcium, acetate of copper, and plumbic salts.

The presence of small quantities of citronellal do not interfere with the detection of citral in the form of citralidenecyanacetic acid. In this manner a mixture of 90 parts of citral and 10 parts of citronellal treated with cyanacetic acid gives a large quantity of a solid product, which, re-crystallised in a mixture of benzene and ligroin, appears in the form of characteristic crystals fusible at 122°.—*Berichte*, 1899, p. 824.

ON THE SEPARATION AND DETERMINATION OF ARSENIC AND ANTIMONY IN ORES.*

By O. C. BECK and H. FISHER.

THIS work was undertaken with the idea of comparing the different known methods, and determining which was the shortest and at the same time the most accurate.

The ore used was an artificial mixture of a native oxide of antimony and a mispickel.

Decomposition of the Ore.

1. This was effected by treating with hydrochloric, nitric, and tartaric acids ("Cairn's Quantitative Analysis, 3rd edition, p. 232); any residue remaining was leached with ammonium polysulphide. The solution was then diluted, and the arsenic and antimony precipitated with hydrogen sulphide. These sulphides were then dissolved in hydrochloric acid and potassium chlorate, and the arsenic and antimony separated by either of the methods which will be given in that section.

2. *Decomposition by means of Caustic Soda* (H. Rose, "Fresenius's Quantitative Analysis, 10th Am. Ed., p. 572). About 5 grms. ore was fused with approximately eight times its weight of sodium hydrate, with a little sodium carbonate and nitrate in an iron dish until completely decomposed. The fusion was allowed to cool and then leached with boiling water and allowed to stand for twenty-four hours with one-third its volume of alcohol. The solution was then filtered and the residue washed, first with alcohol diluted with twice its volume of water, then with a mixture of equal volumes, and finally with a mixture of three volumes of alcohol to one volume of water. To each of these alcoholic solutions a few drops of sodium carbonate solution was added. This treatment converts the arsenic and antimony respectively into soluble sodium arsenate and insoluble sodium metantimonate.

3. *Decomposition by means of Sulphur and Sodium Carbonate* (H. Rose, "Cairn's Quantitative Analysis," 3rd edition, p. 232).—About 0.5 gm. ore was fused with three parts of sodium potassium carbonate and three parts of sulphur, the melt leached with hot water, and filtered from the insoluble residue. This gives the soluble sulpharsenate and sulphantimonate from which the arsenic and antimony are precipitated by acidifying with dilute sulphuric acid. This precipitate was dissolved in hydrochloric acid and potassium chlorate, and the arsenic and antimony separated.

4. *Decomposition by Hydrochloric Acid and Potassium Chlorate* (Pattinson, *Journal Society of Chemical Industry*, vol. xvii., p. 211; and Fischer, *Berichte*, xiii., p. 1778).—From 0.5 to 3 grms. of ore depending upon the amount of arsenic present was dissolved in 30 c.c. concentrated hydrochloric acid and 12 c.c. water, and about five times its weight of potassium chlorate added, heated on the water-bath until the ore was dissolved, and the chlorine driven off. If the potassium chlorate is first placed in the beaker so as to cover the bottom, then the weighed ore placed on this and more chlorate added sufficient to cover the ore and the acid, and water then added, the ore goes into solution more readily than if it is placed directly on the bottom.

5. *Fusion with Sodium Carbonate and Nitrate* (Pearce, *CHEMICAL NEWS*, vol. xlviii., p. 85).—About 0.35 gm. ore was mixed with about ten times its weight of a mixture of one part sodium carbonate to two parts potassium nitrate in an iron dish, and a cover of the same mixture placed over the whole. The contents were gradually heated to fusion and kept in that state for five minutes. The fused mass was cooled, dissolved in water, digested at a boiling temperature for a few minutes, the residue filtered off and washed. This method was modified as follows:—Instead of fusing the ore directly with the carbonate and nitrate mixture, it was first treated on the water-bath in a porcelain crucible with fuming nitric acid and taken to dryness. This treatment was repeated three times. The mass was then mixed with the carbonate and nitrate and treated as described above.

Another modification of this method was tried. A layer of potassium nitrate was fused on the bottom and sides of the iron dish, and on this the mixture of ore and carbonate and nitrate was placed, and the method carried out as before.

Separation of the Arsenic and Antimony.

1. *Fischer Distillation Method*.—The solution of the ore (see 4) or the sulphides dissolved in hydrochloric acid and potassium chlorate (see 3) was placed in a distilling flask connected with a Liebig condenser, which had a delivery tube dipping into a small amount of water contained in a beaker. About 5 grms. of ferrous sulphate were added, and the contents brought up to 150 c.c. with 30 per cent hydrochloric acid, and distilled till only 35 c.c. of the solution remained. The flask was then cooled, the contents again brought up to 150 c.c. with 30 per cent acid and again distilled. This was repeated till the distillate showed no traces of arsenic when tested with hydrogen sulphide. This required six distillations. The arsenic in the distillate and the antimony remaining in the flask were precipitated with hydrogen sulphide.

2. *Pattinson Method*.—The solution (see 4) was filtered on asbestos, and the residue washed thoroughly with a solution of 30 c.c. hydrochloric acid and 12 c.c. water. The arsenic in the filtrate was then reduced by adding small portions of stannous chloride till the solution was colourless, then a slight excess of the chloride was added. Hydrogen sulphide was then immediately passed into the cold solution till saturated. As long as the solution is so strongly acid that it has a specific gravity of 1.16—1.17 arsenious sulphide precipitates free from the sulphides of lead, cadmium, tin, antimony, and bismuth. The solution is stirred and the precipitate settles rapidly; it is then filtered off, washed with a solution of five parts of concentrated hydrochloric acid to two parts of saturated hydrogen sulphide water, and finally with water alone.

3. *Magnesium Ammonium Arsenate Separation*.—The precipitate of arsenic and antimony sulphides (see 3) was dissolved in hydrochloric acid and potassium chlorate, a small amount of tartaric acid added and ammonium hydrate till nearly alkaline. An excess of magnesia mixture was added, and then about one-third of the volume of alcohol, and the solution finally made alkaline with ammonia. The solution was allowed to stand over night, the precipitated magnesium ammonium arsenate filtered

* Contribution from the Havemeyer Laboratories of Columbia University. From the *School of Mines Quarterly*, vol. xx., No. 4.

off, washed with water containing ammonia till the washings showed no opalescence on acidifying with nitric acid and adding silver nitrate. The filtrate was evaporated to small bulk, acidified with hydrochloric acid, and the antimony precipitated with hydrogen sulphide.

Determination of the Arsenic.

1. *Pearce Method.*—To the filtrate (see 5) nitric acid was added till slightly acid, and the solution boiled to expel carbon dioxide and nitrous fumes. It was then neutralised with zinc oxide. A slight excess of the oxide was added, and the solution allowed to stand over night to remove the last traces of acid. An excess of silver nitrate was added, and the solution again allowed to stand over night to insure the complete precipitation of the arsenic. The precipitate was filtered, washed, dissolved in warm dilute nitric acid, and the solution titrated with standardised ammonium sulphocyanate, using ferric alum as indicator. This titration was made in a 250 c.c. bottle provided with a tightly-fitting glass stopper, as it was found that the precipitate of silver sulphocyanate held some of the silver arsenate, for after the solution showed a permanent red colour after merely shaking; when the bottle was stoppered and well shaken the colour disappeared, and it required another 1/10 c.c. before the red colour was permanent on further shaking.

2. *As Magnesium Ammonium Arsenate.*—The sulphide of arsenic, obtained by both the Fischer and Pattinson methods, was dissolved in fuming nitric acid, the nitrous fumes boiled off, the solution diluted, nearly neutralised with ammonia, cooled, one-third of its volume of 95 per cent alcohol added, and magnesia mixture added slowly with stirring, and a few drops more of ammonia, and the whole allowed to stand over night. The precipitate was then filtered on a Gooch crucible, washed with water containing alcohol and ammonia, dried by gradually heating the crucible over the flame and finally ignited, cooled, and weighed as magnesium pyroarsenate.

3. *As Arsenious Sulphide.*—The precipitated sulphide of arsenic was filtered on a Gooch crucible, washed several times with 95 per cent alcohol, once with absolute alcohol, several times with carbon disulphide, again with alcohol, and finally dried in an air-bath at 110° and weighed.

4. *Titration with Iodine.*—The arsenious sulphide, together with the Gooch crucible, was placed in a beaker with a small amount of concentrated sulphuric acid. The beaker was placed in an air-bath and gradually heated to 140–150°, being left uncovered so as to prevent the deposition of sulphur on the sides. As the sulphide dissolved the solution darkened, and it was heated till the colour disappeared and all sulphur dioxide, which would interfere with the subsequent titration, driven off. The solution was removed from the air-bath, diluted and nearly neutralised with sodium carbonate, then sodium bicarbonate was added till the solution contained a slight excess, then titrated with a standardised N/10 iodine solution, using starch as indicator.

Determination of the Antimony.

1. *As Antimonious Sulphide.*—The antimonious sulphide obtained by (1) or (3) under "separation" was filtered on a weighed Gooch crucible, the precipitate washed with 95 per cent alcohol and then with carbon disulphide. The precipitate was then dried at 200° to constant weight.

2. *As Antimonious Antimonic Oxide.*—The antimonious sulphide was filtered on a Gooch crucible and treated with fuming nitric acid till no more sulphur was visible, when the mass was ignited to drive off the excess of nitric and sulphuric acids. A second method of converting the sulphide to the oxide is (Jannasch, "Practischer Leitfaden der Gerichtsanalyse," p. 145) to filter the sulphide on a small paper, wash with a 5 per cent solution of ammonium nitrate containing hydrogen sulphide. Dry the precipitate, separate it as much as possible from the paper, and

place in a small weighed porcelain crucible (50–70 c.c.). Spread the paper on a watch-glass, wash it thoroughly with hot ammonium sulphide, and then with boiling water. Evaporate the solution on a water-bath to dryness, add fuming nitric acid till no more sulphur is visible, then ignite.

3. *Weller Method (Liebig's Annalen, ccxiii., p. 364).*—*Titration of Liberated Iodine.*—The residue obtained by leaching the fusion of Rose's method (see (2) under "decomposition"), which consisted of ferric oxide and sodium hydrogen metantimonate, was dissolved in hydrochloric acid and potassium chlorate. The antimony was then precipitated as sulphide by means of hydrogen sulphide to separate it from the iron and filtered. It was then dissolved in hydrochloric acid and potassium chlorate, and the chlorine and oxides of chlorine driven off by heating on a water-bath or by gently boiling. The solution was diluted to about 200–300 c.c., 5 grms. of potassium iodide added, and the iodine titrated with standard thiosulphate after adding starch solution. The thiosulphate solution used was standardised against copper and calculated to its equivalent in antimony.

4. *Mohr's Method.*—Titration with iodine ("Mohr's Titrimethode"; and Clarke, *J. S. C. I.*, vol. xv., p. 255). The sodium hydrogen metantimonate obtained by fusion was dissolved in hydrochloric acid and potassium chlorate, the antimony precipitated as sulphide and again dissolved as in the previous method. The antimonic chloride was then reduced to antimonious chloride by means of a sulphurous acid. The excess of acid was then boiled out, 1 to 2 grms. of tartaric acid added, the solution neutralised with sodium carbonate, and 20–30 c.c. of a saturated solution of sodium bicarbonate added, and the solution titrated at a bulk of 200–300 c.c. with standard N/10 iodine, using starch as indicator.

The results obtained by these methods were as follows:—

Arsenic.				
Pearce method	—	15.83	15.94	
Pearce method, nitric acid modification	—	16.03	16.17	
Pearce method, potassium nitrate modification	—	16.18	16.37	
Fischer method	—	16.25	16.38	
Pattinson method, iodine titration	—	16.23	16.34	
Pattinson method, magnesium pyroarsenate	—	16.23	16.32	
Pattinson method, arsenious sulphide	—	16.69	16.94	

Antimony.				
As antimonious sulphide	18.74	18.91	—	Jannasch mod.
As antimonious antimonic oxide	17.85	17.96	18.02	
By Weller method	18.12	18.09	18.16	
By Mohr's method	18.31	18.19	18.26	

It will be seen from the table that the ordinary Pearce method and the nitric acid modification give slightly low results. This is probably due to a slight loss of arsenic by volatilisation. The potassium nitrate method, while accurate, takes too long.

The Fischer distillation method gives good results, but is also too long.

The Pattinson method is preferable to the other two on account of its accuracy and rapidity, especially when the sulphide is titrated with iodine. When the arsenic is weighed as sulphide the results are high, probably due to the impossibility of completely dissolving the sulphur out of the precipitate.

In regard to the antimony the sulphide also gives high results.

The oxide gave slightly low results due to the unavoidable spattering on treating the sulphide with the nitric acid. Jannasch's modification, while giving slightly higher results, requires a longer time, and introduces a large

amount of sulphur which must all be oxidised before ignition.

The Weller and Mohr methods gave results which agreed closely.

The writers thank Dr. E. H. Miller for his kind assistance throughout this work.

ON A POSSIBLE HYDRIDE OF MAGNESIUM.

(PRELIMINARY NOTE).

By WM. FRENCH, M.A., F.I.C.

WHEN hydrogen gas, made by the action of cold water on magnesium, is burned, it does so with a very peculiar green flame, and as this has been observed so many times I was led to investigate the cause. The same green colour is observable with the gas obtained by the action of HCl on the metal, but in a lesser degree. Below I give a few preliminary experiments which have been repeated with metal from different sources. Further experiments are now in progress, and Prof. G. D. Liveing, F.R.S., has kindly offered to examine the flame spectroscopically, and compare it with the lines obtained by him when sparking magnesium in hydrogen (*Proc. Roy. Soc.*, 1881).

The gas gives a blackish precipitate with silver nitrate, but in such a small quantity that sufficient has not yet been obtained for an analysis. When the gas is burned at a jet, and a piece of cold porcelain held in it, the flame assumes a beautiful green colour, and with the spectro-scope I have by me (which is only a model home-made one) I obtain a green band which looks as if it might be due to magnesium. When the porcelain is not allowed to get too hot a metallic mirror is produced, which very quickly becomes oxidised and white. This again has only been obtained in such small quantities that it has not been fully examined. When the gas is passed through a hot glass tube, on some occasions a deposit has been obtained, and on others I have not been able to get any.

Experiments are in progress to isolate the body, which it seems to me may possibly be a hydride of magnesium.

Grammar School, Bury.

Transformation of Styrolene into Metastyrolene under the Influence of Light.—Georges Lemoine.—Styrolene or cinnamene, C_8H_8 , is changed by heat in the dark into a polymer, metastyrolene. This same polymerisation is produced at ordinary temperatures by solar light, but takes place slowly, the mixture remaining homogeneous on account of the metastyrolene dissolving in excess of styrolene. The author's experiments show that in the two cases the part played by the light is that of accelerating an exothermic transformation, which would be produced in darkness at the same temperature, but very much more slowly.—*Comptes Rendus*, vol. cxxix., No. 19.

Dioxide of Molybdenum.—Marcel Guichard.—The author obtains this oxide by two distinct methods: (1) by the action of molybdic anhydride on ammonium molybdate, and (2) by the electrolysis of fused molybdic anhydride. In both cases the oxide obtained was pure and crystallised, analysis showing it to have the formula MoO_2 . This research also shows that there is not known another anhydrous oxide of molybdenum, intermediate between the oxides MoO_2 and MoO_3 , except that which results from the dehydration of the blue hydrated oxide, if, however, this dehydration can be effected without peroxidation.—*Comptes Rendus*, vol. cxxix., No. 19.

THE VARIATION IN THE COMPOSITION OF "PARIS GREEN," WITH SCHEME FOR ANALYSIS.*

By THOMAS B. STILLMAN, Ph.D.

(Concluded from p. 251).

THE chemical examination of pure Paris green is comparatively simple, since it is soluble in slight excess of ammonia, forming a dark blue solution. If it be desired to determine the amount of As_2O_3 , a rapid and accurate method is by the use of a standard solution of potassium bichromate, whereby arsenious acid, in acid solution, is oxidised to arsenic acid by the bichromate. The bichromate solution should be of such strength that 1 c.c. of it corresponds to 0.00495 gm. As_2O_3 . Full instructions for this method will be found in Sutton's "Volumetric Analysis," p. 138. If arsenic acid is present in the Paris green, its amount can be determined as follows:—Dissolve a sample of the green in dilute hydrochloric acid, pass H_2S gas through the solution until saturated, keeping the temperature of the liquid at about $70^\circ C$. Filter, wash the sulphide of arsenic thoroughly with water containing H_2S , transfer precipitate and filter to a flask; add excess of saturated solution of mercuric chloride in HCl (1.12 sp. gr.), and warm until a white precipitate forms, water being added until the volume of HCl in the liquid amounts to about one-sixth. Add excess of standard bichromate solution from a burette, and determine excess over that required to oxidise the arsenious acid by means of standard solution of ferrous sulphate. By this operation the total arsenic in the Paris green is determined as As_2O_3 . If, now, the amount already existing as As_2O_3 be found and subtracted from the total As_2O_3 , the difference should be calculated to As_2O_5 —which would be the amount of arsenic acid desired.

The chemical examination of Paris green containing other pigments may or may not be a complex undertaking, depending upon the number of added materials.

The accompanying scheme of analysis, arranged for this purpose, will probably include all varieties of Schweinfurt green.

The following references will be found of service in this connection:—

- Manufacture of Paris Green from Scheele's Green by Addition of Acetic Acid (S. Camille Koehlin, *Journ. Soc. Chem. Industry*, v., 596).
- Method of Manufacture of Paris Green (Ost, "Technische Chemie," 502).
- Estimation of Copper in Paris Green (Böckmann, "Chemisch-Technische Untersuchungsmethoden," ii., p. 195).
- Microscopical Examination of Paris Green ("Untersuchungsmethoden," ii., p. 196).
- Manufacture of Schweinfurt Green ("Muspratt's Chemistry," vol. i., p. 220).
- "Century Dictionary," iii., article relating to green pigments.
- Die Mikroskopische Untersuchung des Schweinfurter Grüns und seine Bildung (Sattler, *Zeit. Anal. Chem.*, 2 S., 35).
- Le vert de Schweinfurt (Köehlin, *Bull. Mulhouse*, 56 S., 444).
- Das Schweinfurter Grün und seine Schicksale (Koller, *Gew. Zeit.*, 49 S., 102; *Ind. Zeit.*, 25 S., 265).
- Prüfung arsenhaltiger Farben und Tapeten (Reichardt, *Apoth. Zeit.*, 4 S. 226).

SCHEME FOR ANALYSIS OF "PARIS GREEN"

CONTAINING

BaSO₄, PbSO₄, 3CuOAsO₃Cu(C₂H₃O₂)₂, PbCrO₄, ZnO, and CaCO₃.

Add excess of dilute nitric acid, warm, filter, and wash well with hot water.

<p><i>Residue</i> { BaSO₄, PbSO₄.</p> <p>Transfer to a No. 3 beaker, add excess of a saturated solution of ammoniac acetate; warm ten minutes, filter, wash with hot water.</p>	<p><i>Residue</i>, PbSO₄.</p> <p>Dry, ignite, and weigh as PbSO₄, and calculate to PbCrO₄.</p>	<p><i>Solution</i>.</p> <p>Add excess of dilute H₂SO₄, evaporate to dryness; add dilute H₂SO₄, warm, filter, wash with hot water, dry, ignite, and weigh as PbSO₄.</p>	<p><i>Residue</i>, BaSO₄.</p> <p>Dry, ignite, and weigh as BaSO₄.</p>	<p><i>Residue</i>, CuS</p> <p>Transfer to a No. 3 beaker, add excess of strong solution of sodium sulphide, warm gently ten minutes, filter, wash with water.</p>	<p><i>Residue</i>, CuS.</p> <p>Dissolve in nitric acid, dilute with water, filter off any separated sulphur, and determine copper by electrolysis, (See "Stillman's Engineering Chemistry," p. 5).</p>	<p><i>Solution</i>.</p> <p>Acidify with HCl, pass H₂S gas to saturation, filter, wash with H₂S water, and determine arsenic by method of Kessler. (See "Sutton's Volumetric Analysis," p. 138).</p>	<p><i>Residue</i>, ZnS.</p> <p>Dissolve precipitate in HCl, dilute with water, boil, add gradually slight excess of sodium carbonate; boil three minutes, filter, wash thoroughly with hot water, dry, ignite, and weigh as ZnO.</p>	<p><i>Solution</i>.</p> <p>Boil to expel the H₂S, add a few drops of ammoniac hydrate, then excess of solution of ammoniac oxalate. Set aside two hours, filter, wash with water containing $\frac{1}{10}$ volume of ammoniac hydrate, dry, ignite, and weigh as CaO, and calculate to CaCO₃.</p>
<p><i>Solution</i>.—Add slight excess of dilute H₂SO₄, evaporate nearly to dryness, allow to cool, add dilute H₂SO₄, warm, filter, and wash well with water.</p>	<p><i>Residue</i>, PbSO₄.</p> <p>Dry, ignite, and weigh as PbSO₄, and calculate to PbCrO₄.</p>	<p><i>Solution</i>.—Pass H₂S gas through the liquid to saturation, keeping the temperature of the solution at about 70° C. Filter, wash with water containing H₂S.</p>	<p><i>Residue</i>, Cr₂(OH)₆.</p> <p>Dry, ignite, and weigh as Cr₂O₃. Calculate to—PbCrO₄.</p>	<p><i>Residue</i>, ZnS.</p> <p>Dissolve precipitate in HCl, dilute with water, boil, add gradually slight excess of sodium carbonate; boil three minutes, filter, wash thoroughly with hot water, dry, ignite, and weigh as ZnO.</p>	<p><i>Solution</i>.—Pass H₂S gas to saturation, filter, wash with water containing a few drops of ammoniac sulphide.</p>	<p><i>Solution</i>.</p> <p>Boil to expel the H₂S, add a few drops of ammoniac hydrate, then excess of solution of ammoniac oxalate. Set aside two hours, filter, wash with water containing $\frac{1}{10}$ volume of ammoniac hydrate, dry, ignite, and weigh as CaO, and calculate to CaCO₃.</p>	<p><i>Residue</i>, ZnS.</p> <p>Dissolve precipitate in HCl, dilute with water, boil, add gradually slight excess of sodium carbonate; boil three minutes, filter, wash thoroughly with hot water, dry, ignite, and weigh as ZnO.</p>	<p><i>Solution</i>.</p> <p>Boil to expel the H₂S, add a few drops of ammoniac hydrate, then excess of solution of ammoniac oxalate. Set aside two hours, filter, wash with water containing $\frac{1}{10}$ volume of ammoniac hydrate, dry, ignite, and weigh as CaO, and calculate to CaCO₃.</p>

(a) If a white precipitate forms, of zinc hydroxide, add ammoniac hydrate until it dissolves. If it be desired to determine the acetic acid, another portion of the Paris green should be taken, and tested by C. Mohr's process. (Consult page 82, "Sutton's Volumetric Analysis").

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

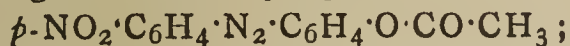
Ordinary Meeting, November 2nd, 1899.

Dr. W. H. PERKIN, F.R.S., Vice-President, in the Chair.

(Concluded from p. 254).

132. "Notes on Polyazo-compounds." By RAPHAEL MELDOLA and WILLIAM ARTHUR WILLIAMS.

Paranitrobenzene azophenol (Meldola, *Trans.*, 1885, xlvii., 658) melts at 213–216° if the temperature of the bath is raised rapidly. The melting-point formerly given (184°) is erroneous, and the error has been corrected in the latest edition of Beilstein (vol. iv., p. 1410). The compound has been further characterised by its benzoyl and acetyl derivatives: — $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$; slender, orange needles, m. p. 195°.



dull, orange needles, m. p. 147°. The corresponding amidobenzeneazophenol melts at 186° (181° in original description), and forms a difficultly soluble sulphate crystallising in silvery scales having the formula $(p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH})_2\cdot\text{H}_2\text{SO}_4\cdot 3\text{H}_2\text{O}$.

The base, on acetylation with acetic anhydride and sodium acetate, gives a mixture of a diacetyl with a monacetyl derivative, the latter being phenolic in character: $\text{C}_2\text{H}_3\text{O}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$; minute, dull orange needles, m. p. 203°; $\text{C}_2\text{H}_3\text{O}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_2\text{H}_3\text{O}$; bright, orange scales, m. p. 236–237°.

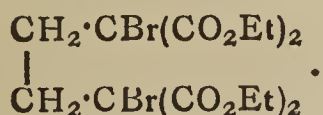
The disazo-compound, $\text{C}_6\text{H}_4(\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH})_2$ (Meldola, *loc. cit.*, 659), does not appear to be crystallisable. Boiling with acetic anhydride and dry sodium acetate results in the formation of the diacetyl derivative, $\text{C}_6\text{H}_4(\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_2\text{H}_3\text{O})_2$, which crystallises from nitrobenzene in small golden-yellow plates melting at 246–248°.

The amidobenzeneazophenol (m. p. 168°) obtained by Wallach and Schulze (*Ber.*, 1882, xv., 3021) by removing the acetyl group from the corresponding acetamido-compound, is the meta-compound isomeric with our para-compound (m. p. 186°).

Para-amidobenzeneazophenol, when treated at a low temperature with a mixture of dilute sulphuric acid and sodium dichromate, undergoes fission in a remarkable way. The azo-group remains attached to the $\text{NH}_2\cdot\text{C}_6\text{H}_4$ -residue with the formation of a diazodichromate of the complex $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2$ — and the simultaneous oxidation of the $\text{C}_6\text{H}_4\cdot\text{OH}$ residue to quinone. This mode of decomposition of azo-compounds is being further investigated.

133. "On Ethyl Dibromobutanetetracarboxylate and the Synthesis of Tetrahydrofurfuran- $\alpha\alpha'$ -dicarboxylic Acid." By BEVAN LEAN, D.Sc., B.A.

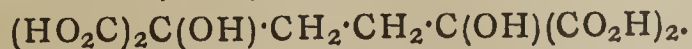
A solution of ethyl butanetetracarboxylate in chloroform is readily acted on by bromine with the formation of ethyl- $\alpha\alpha'$ -dibromobutanetetracarboxylate,—



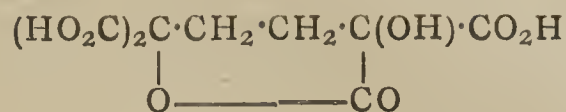
The crystalline dibromo-compound (m. p. 83°) thus obtained, when digested for some hours with a strong solution of barium hydroxide, yields an insoluble barium salt of dihydroxybutanetetracarboxylic acid,—



If this salt is decomposed by sulphuric acid, there results a solution of dihydroxybutanetetracarboxylic acid,—

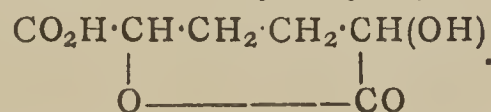


On slowly concentrating the very acrid aqueous solution of this substance over strong sulphuric acid, long needles were obtained of the monolactone,—

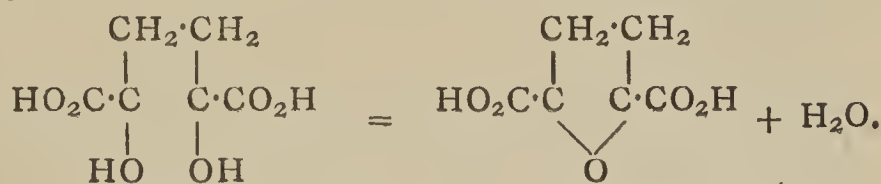


The silver salt of this substance ($\text{C}_8\text{H}_8\text{O}_9$) was prepared and has the composition $\text{C}_8\text{H}_6\text{Ag}_4\text{O}_{10}$. The substance, therefore, readily takes up again the elements of water, as is customary with δ -lactones. It begins to soften at 145°, and at 156° fusion is complete and carbon dioxide is evolved.

On heating an aqueous solution of this lactone in a sealed tube at 150°, the acid is decomposed with elimination of carbon dioxide. If the aqueous solution be evaporated to a small bulk and placed over sulphuric acid, small star-shaped clusters of crystals gradually appear, and eventually the whole becomes solid. The product is found to have the composition $\text{C}_6\text{H}_8\text{O}_5$, which is that of dihydroxyadipic acid less one molecule of water, and the simplest explanation would be that the substance is the δ -lactone of dihydroxyadipic acid, viz.,—



But careful examination shows that this is not so, for the silver salt was prepared and found to have the composition $\text{C}_6\text{H}_6\text{Ag}_2\text{O}_5$. Further investigation shows that the elimination of water takes place between the two hydroxyl-groups, and that the substance is tetrahydrofurfuran- $\alpha\alpha'$ -dicarboxylic acid, formed thus:—



This substance begins to melt at 65°, but fusion proceeds only gradually, and is not complete till about 120°. The absence of a definite melting-point pointed to it being a mixture of stereoisomeric acids, and experiments were made to separate them by fractional crystallisation from water.

A higher melting tetrahydrofurfuran $\alpha\alpha'$ -dicarboxylic acid, ($\text{C}_6\text{H}_8\text{O}_5$), m. p. 123–125°, was isolated, and also crystals melting at 63–64°, which had the composition $\text{C}_6\text{H}_{10}\text{O}_6$. This latter substance was at first supposed to be dihydroxyadipic acid, but the silver salt was prepared and found to be $\text{C}_6\text{H}_6\text{Ag}_2\text{O}_5$, a result which led to the conclusion that the substance was the isomeric monohydrate of tetrahydrofurfurandicarboxylic acid.

When the substance $\text{C}_6\text{H}_{10}\text{O}_6$ (m. p. 63–64°) was placed for some days over strong sulphuric acid, the product melted at 93–95°, and it then had the composition $\text{C}_6\text{H}_8\text{O}_5$. Its silver salt was $\text{C}_6\text{H}_6\text{Ag}_2\text{O}_5$, confirming the conclusion that the substance $\text{C}_6\text{H}_8\text{O}_5$ (m. p. 93–95°) was a lower melting tetrahydrofurfuran- $\alpha\alpha'$ -dicarboxylic acid. It reverts to the monohydrate when exposed in the air.

This case of geometrical isomerism would appear to be the first one established in the furfuran series.

The author also discusses and criticises F. Tiemann's work on isosaccharic acid and "norisosaccharic acid," and shows that all the derivatives of these two acids which he has described are probably derivatives of $\beta\beta'$ -dihydroxytetrahydrofurfuran- $\alpha\alpha'$ -dicarboxylic acid.

134. "The Application of Powerful Optically Active Acids to the Re-solution of Externally Compensated Basic Substances. Re-solution of Tetrahydroquinaldine." By WILLIAM JACKSON POPE and STANLEY JOHN PEACHEY.

In continuation of previous work (*Proc.*, 1899, xv., 124) the authors find that dextrotetrahydroquinaldine cannot be prepared in quantity in a pure condition from the dextrocamphor sulphonate nor the hydrochloride of the crude dextro-base obtained from the inactive base; the benzoyl-derivative of the dextro-base can be easily isolated from the crude dextro-base, and on hydrolysis with hydrochloric acid yields the dextro-base in a pure state.

The following molecular rotations, determined in dilute aqueous solution, are closely related in that the values for the first two salts can be calculated directly from those of the third and fourth:—

Dextrotetrahydroquinaldine dextrocamphorsulphonate,
 $[M]_D = +173.3^\circ$.

Lævotetrahydroquinaldine dextrocamphorsulphonate,
 $[M]_D = -69.5^\circ$.

Lævotetrahydroquinaldine hydrochloride, $[M]_D = -121.7^\circ$.

Ammonium dextrocamphorsulphonate, $[M]_D = +51.7^\circ$.

135. "The Application of Powerful Optically Active Acids to the Re-solution of Feebly Basic Substances. Re-solution of Camphoroxime." By WILLIAM JACKSON POPE.

The only basic substances hitherto resolved into optically active compounds by crystallisation with an optically active acid have been powerful bases, because feeble bases do not form stable salts with tartaric acid. By using a powerful optically active acid, however, feebly basic externally compensated substances, such as oximes, may be resolved. Thus by fractionally crystallising a mixture of racemic camphoroxime with Reychler's dextrocamphorsulphonic acid from a solution in acetone or ether, the isomeric salts, *dextrocamphoroxime dextrocamphorsulphonate* and *lævocamphoroxime dextrocamphorsulphonate*, $C_{10}H_{16}NOH, C_{10}H_{15}OSO_3H, H_2O$, may be isolated; the former has the specific rotation $[\alpha]_D = +4.3^\circ$, whilst the latter gives $[\alpha]_D = +41.7^\circ$. Both salts are decomposed by water, yielding the corresponding optically active camphoroximes.

136. "The Application of Powerful Optically Active Acids to the Re-solution of Externally Compensated Basic Substances. Re-solution of Tetrahydroparatoluquinaldine." By WILLIAM JACKSON POPE and EDMUND MILTON RICH.

In continuation of previous work (*Proc.*, 1899, xv., 171) the authors have isolated *dextrotetrahydroparatoluquinaldine* as its hydrochloride from the mother-liquors remaining after separating the lævo-isomeride as dextro-bromocamphorsulphonate from the externally compensated base; the hydrochloride of the new base crystallises in sphenoidally hemihedral orthorhombic crystals containing one molecule of water. The optically active bases themselves crystallise from light petroleum solutions in hemimorphic monosymmetric prisms.

137. "Homogeneity of Dextrolævo- α -phenethylamine Dextrocamphorsulphonate." By WILLIAM JACKSON POPE and ALFRED WILLIAM HARVEY.

Externally compensated α -phenethylamine combines with Reychler's dextrocamphorsulphonic acid, yielding *dextrolævo- α -phenethylamine dextrocamphorsulphonate*, $CH_3 \cdot CH(Ph) \cdot NH_2, C_{10}H_{15}OSO_3H$, which crystallises from acetone in minute colourless prisms melting at $141-143^\circ$. The salt has the molecular rotation $[M]_D = +51.5^\circ$ in dilute aqueous solution, and since ammonium dextrocamphorsulphonate gives $[M]_D = +51.7^\circ$ in aqueous solution, the new salt belongs to the class of partially racemic substances discovered by Ladenburg. Externally compensated α -phenethylamine platinochloride, $(CH_3 \cdot CH(Ph) \cdot NH_2)_2, H_2PtCl_6$, crystallises in golden-yellow scales melting at $213-214^\circ$.

138. "The Characterisation of Racemic Liquids." By FREDERIC STANLEY KIPPING and WILLIAM JACKSON POPE.

It is shown that the results obtained by Ladenburg's latest method (*Ber.*, 1899, xxxii., 1822) for discriminating between "racemic" and "non-racemic" liquids have no bearing upon the question they are supposed to answer.

Series of experiments have further been made to determine the equilibrium between mixtures of dextro- and lævo-pinene in various proportions and their solutions in ethyl and methyl alcohol. It is shown that the distribution ratio of the excess of one antipodes over the other in the oil and in the alcoholic solution in contact with it is nearly independent of the concentration of that excess. This behaviour is explained by Nernst's distribution law,

and would be expected with both racemic and non-racemic substances.

Experiments with dextro- and lævo-camphorsulphonic chlorides are also described, which show the fallacious nature of the conclusions drawn by the application of Ladenburg's method.

139. "A Method for discriminating between 'Non-racemic' and 'Racemic' Liquids." By WILLIAM JACKSON POPE and STANLEY JOHN PEACHEY.

The densities of lævo- and externally compensated tetrahydroquinaldine are the same under similar conditions, namely, $d_{t_4} = 1.01930 + 0.00079(20 - t)$ between 14° and 21° ; their molecular refractions are also the same, the observed values being—

$$M_D = 47.50$$

for the active, and—

$$M_D = 47.57$$

for the inactive base. These numbers afford no evidence that the inactive liquid base is racemic.

The variations in specific rotation of non-electrolytes dissolved in various solvents are traced, in the main, to variations in the association factor of the dissolved substance, and it is shown that the highly associated lævotetrahydroquinaldine has specific rotations varying from $[\alpha]_D = -46^\circ$ to -118° in different solvents. On dissolving the base in solvents having nearly its own association factor, such as tetrahydroquinoline, the specific rotation of the active base remains nearly the same as in the solvent free-state, because its association factor remains nearly unchanged; lævotetrahydroquinaldine, when dissolved in the externally compensated base as solvent, has practically the same specific rotation as in the pure liquid state, namely, $[\alpha]_D = -58.12^\circ$. It follows that externally compensated tetrahydroquinaldine has the same molecular weight in the liquid state as its active components, and consequently cannot be a racemic compound.

It is shown that the specific rotation of lævopinene, an unassociated liquid, changes comparatively slightly with the solvent, and that it has the same specific rotation when dissolved in the externally compensated hydrocarbon as when in the pure liquid state. Inactive pinene is therefore not racemic.

The authors conclude that the above results afford the first method for discriminating between racemic and non-racemic liquids which has yielded positive results.

140. "On Two Hydrated Cobalt Oxides, Green- and Buff-coloured." By W. N. HARTLEY, F.R.S.

The preparation and analysis of two hydrated cobalt oxides is described. The green compound was formed when a cold solution of cobalt chloride was precipitated by an equivalent quantity of barium hydroxide, both solutions having been boiled, and a Torricellian vacuum being maintained in the precipitating vessels. Its formula is $Co_3O_4, 6H_2O$. The buff-coloured compound resulted when the precipitation was carried out in like manner, but with excess of barium hydroxide. Its composition is $Co_8O_9, 11H_2O$.

The action of acetic acid on the green hydrate separates a brown oxide already known as Co_3O_4 . There was a similar action and the separation of black oxide from the buff-coloured hydrate. This points to the following formulæ:—Green hydrate, $Co_2O_3, Co(OH)_2, 5H_2O$. Buff hydrate, $Co_2O_3, 6Co(OH)_2, 5H_2O$. These are distinct compounds, and not merely mixtures.

141. "A Method of Separating Isomeric Xylidines from the Commercial Product." By W. R. HODGKINSON and L. LIMPACH.

This method depends on the fact that acetate of meta-(Me : Me : $NH_2 = 1 : 3 : 4$)-xylidine crystallises very readily when the crude mixture is treated with acetic acid. From the filtrate from this acetate, hydrogen chloride precipitates the para-(Me : NH_2 : Me = $1 : 2 : 4$)-xylidine as hydro-

chloride, and the filtrates from this, on concentration and heating, yields up the hydrochloride of the (Me:NH:Me = 1:2:3)-xylidine as a crystalline sublimate. The residue of hydrochlorides of the two ortho-(Me:Me:NH₂=1:2:3) and (Me:Me:NH₂=1:2:4)-xylidines is hydrolysed and the bases converted into formyl derivatives; that from the (Me:Me:NH₂=1:2:3)-base crystallises moderately easily, whilst the other from the (Me:Me:NH₂=1:2:4) base is exceedingly difficult to obtain as a solid.

142. "Action of Hydrolytic Agents on α -Dibromocamphor, and the Constitution of Bromocamphorenic Acid." By ARTHUR LAPWORTH.

In addition to the experiments already briefly described (*Proc.*, 1899, xv., 161), the paper gives an account of the behaviour of α -dibromocamphor towards hydrolytic agents other than moist silver compounds. It is found that this substance is readily attacked by mercurous nitrate dissolved in boiling acetic acid, and that a small quantity of bromocamphorenic acid is obtained. It is not attacked by lead compounds under these conditions, and chars when heated with water and lead oxide in closed tubes to 120—150°; in the latter case, no bromocamphorenic acid could be detected, but a small quantity of camphoric acid, and in one instance a minute quantity of camphorquinone, was found to be produced.

The action of oxidising agents on dibromocampholid, bromocamphorenic acid, α -monobromocampholid, and other derivatives of camphorenic acid has been investigated. It is found that in each case where oxidation occurs nearly pure homocamphoronic acid is obtained, an excellent yield of the latter substance being produced when α -monobromocampholid is oxidised with dilute nitric acid and silver nitrate.

PHYSICAL SOCIETY.

Ordinary Meeting, November 24th, 1899.

Prof. G. CAREY FOSTER, F.R.S., Vice-President, in the Chair.

A PAPER "On the Conductivities of certain Heterogeneous Media for a Steady Flux having a Potential" was read by Dr. C. H. LEES.

Two formulæ have already been proposed to express the conductivity of a mixture in terms of the conductivities of its constituents. In the first formula the conductivity is represented as the sum of a number of terms each one of which is the product of the conductivity of any constituent and the fractional part of the mixture which is made up of that constituent. In the second formula the resistivity of a mixture is expressed in the same way with respect to the resistivities and percentages of its constituents. In general the first of these suppositions gives results which are above the experimental values, while the second gives results which are below. If we suppose that the mixture is made up of a series of columns of the separate parts stretching normally between two equipotential surfaces, then the conductivity would be accurately represented by the first formula. If, however, we assume that the constituents are arranged in parallel layers, then the second formula would apply. In the present paper the author has attacked the problem two-dimensionally, and has investigated the relation which holds between the conductivities when the constituents are arranged in the mixture alternately, like the squares on a draught-board. Dealing first with two components, it is easily shown that the problem reduces itself to finding the form of the equipotential curves and of the stream lines in a square which is divided by a diagonal into two parts of different material. By means of conformal representation, Dr. Lees has referred the square under consideration to a kite-shaped quadrilateral with two opposite angles right angles, and the other two so determined by the conductivities of the constituents as to

give straight equipotential lines in the two portions of the figure which represent the two materials, and which are separated the one from the other by the axis of symmetry. The general relation which exists between the vector coordinates in the two systems has been proved by Love to consist of elliptic functions, but near the angular points of the figures a close approximation can be obtained by the use of a simple exponential expression. Taking the known solution to the problem in the case of the kite-shaped quadrilateral, it is easy to calculate the result for the square under consideration. This leads to the conclusion that the conductivity of the square is the geometric mean of the conductivities of the constituents. Allowing the medium to become fine-grained, and introducing new materials, it follows at once that the logarithm of the conductivity of a mixture is equal to the sum of a number of terms, each one of which is the product of the logarithm of the conductivity of any constituent and the fractional part of the mixture which is made up of that constituent. By a superposition of fluxes the author has shown that the above law holds for flows in four directions, and he therefore considers that with the assumed structure the formula represents the conductivity for any flux.

Dr. LEES then read a second paper, "On the Thermal Conductivities of Mixtures and their Constituents."

In this paper the three formulæ considered in the preceding communication are applied to the known experimental results upon the conductivities of mixtures of liquids. The author finds that the least satisfactory formulæ is the first one, whereas the least unsatisfactory is the logarithmic one.

Mr. APPLEYARD said that it was frequently of importance to be able to determine the resistance of a mixture of gutta-perchas from the known resistances of component parts. He had attempted, without success, to do this by means of the old formulæ, and he would be interested to see whether Dr. Lees' logarithmic formula gave better results. In electrical work Mr. Appleyard pointed out that the nature of the contacts affected the conductivity, the resistance of a sheet of rubber being different when measured between metal plates and mercury sheets.

Mr. CAMPBELL said that the difference between the calculated and observed results might be due to the thermoelectric properties of the materials. Lord Rayleigh had observed that the high resistivity of alloys might be due to a back E.M.F. produced by the contact of dissimilar metals. Mr. Campbell said that he had measured the resistances of ferro-nickels both with direct and alternative currents, and found them the same in the two cases.

In reply, Dr. LEES said that all his experimental work on conductivity had been carried out with mercury contacts.

The Society then adjourned until December 8th, when, by the invitation of Prof. S. P. Thompson, the Meeting will be held in the Physical Laboratory of the Finsbury Technical College.

CORRESPONDENCE.

THE PERIODICITY OF MELTING- AND BOILING-POINTS.

To the Editor of the Chemical News.

SIR,—With every new property of a body which can in any way help the establishment of the Periodic Law, there always arises the question of the periodicity of melting- and boiling-points.

One fact seems to have always been neglected in discussing this point. When we speak of the melting- or boiling-point of an element or compound, we always measure from some arbitrary zero. For instance, water boils at 100° C., and mercury at 360° C.; that is, 100°

Compound.	M.-p.	B.-p. (at 15 m.m.).	B.-p.—M.-p.	Difference.
C ₂₀ H ₄₂ ..	36.7	205	168.3	6.3
C ₂₁ H ₄₄ ..	40.4	215	174.6	
C ₂₂ H ₄₆ ..	44.4	224.5	180.1	5.5
C ₂₃ H ₄₈ ..	47.7	234	186.3	
C ₂₄ H ₅₀ ..	51.1	243	191.9	6.2
C ₂₅ H ₅₂ ..				
C ₂₆ H ₅₄ ..				5.6
C ₂₇ H ₅₆ ..	59.5	270	210.5	
C ₂₈ H ₅₈ ..				5.86
C ₂₉ H ₆₀ ..				
C ₃₀ H ₆₂ ..				17.58
C ₃₁ H ₆₄ ..	68.1	302	234.9	
C ₃₂ H ₆₆ ..	70	310	240	18.6
C ₃₃ H ₆₈ ..				
C ₃₄ H ₇₀ ..				22.44
C ₃₅ H ₇₂ ..	74.7	331	256.3	
And—				24.4
C ₁₇ H ₃₆ ..	22.5	303	270.5	
C ₁₈ H ₃₈ ..	28	317	279	5.1
C ₁₉ H ₄₀ ..	32	330	298	

and 360° above 0, this particular zero being the melting-point of water. But this temperature 0° C. does not treat mercury in the same way as it treats water. At 0° C., water is in a condition corresponding to that of mercury at -9° C. In the history of chemistry there has been a case analogous to this, namely in the "law of Dulong and Petit," where carbon, boron, and silicon did not give the same atomic heat as the other elements until the specific heat was taken in each case at a temperature approximately similarly distant from its melting-point.

So, in the case of melting- and boiling-points, the apparently only fair way of considering the matter is by comparing the number of heat units between the melting- and boiling-points. By this means we get a range of temperature which is similar in each case.

Taking the cases of sodium and potassium, cadmium and mercury, tin and lead, we get—

Element.	M.-p.	B.-p.	B.-p.—M.-p.
Na	96.9	818.5	721.6
K	60.2	693	635.5
Cd	320	763.7	443.7
Hg	-9	360	369
Sn	229	1525	1296
Pb	330	1525	1195

Then—

Boiling-point—melting-point (Na : K :: Cd : Hg :: Sn : Pb)

$$722 : 636 :: 444 : 369 :: 1296 : 1195$$

$$1 : 0.881 :: 1 : 0.831 :: 1 : 0.922$$

These results seem fairly agreeable, especially as the temperatures are only a rough average of the values found in Landolt's tables.

If the elements above mentioned are, indeed, so to say, corresponding, then—

Atomic weight (Na : K :: Cd : Hg :: Sn : Pb)
should hold good.

$$23 : 39 :: 118 : 200 :: 119 : 206$$

$$1 : 1.7 :: 1 : 1.7 :: 1 : 1.7.$$

It is, however, a curious thing that sodium and potassium, which are adjacent to each other in Mendeleeff's table, and the two pairs—cadmium and mercury, tin and lead—which are set down as having some other unknown element between them, should have similar atomic weights and similar differences in boiling- and melting-points.

Equally noticeable is the difference in boiling-point—melting-point that an increase or decrease of -CH₂ makes in homologous series of organic compounds. (See Table, preceding column).

Seeing that, in taking melting- and boiling-points of organic compounds, discrepancy usually occurs, owing to the different methods of different observers, these numbers may be taken as fairly concordant.

It is evident that the increment for -CH₃ might also be found in compounds, or any other group, providing the group is similarly added.

This, then, might be a useful means for checking the constitution of compounds.—I am, &c.,

ALFRED WERTHEIMER,

Laboratory of the Stirling Chemical Works,
Stratford, London, E., Nov. 21, 1899.

DETERMINATION OF CARBON IN IRON AND STEEL WITHOUT ABSORPTION APPARATUS.

To the Editor of the Chemical News.

SIR,—I am not disposed to disagree with Mr. Dougherty if he considers the respective factors given by Schützenberger, Zaboudsky, and Blair to be confirmatory of his own. There are analysts, however, to whom such differences are important, and I had no wish further than to draw their attention to them.

"If the carbonaceous compounds," says Mr. Dougherty, "were soluble in warm dilute nitric acid, how is it that the factor is only 67.5, instead of much higher, in order to compensate for the alleged loss?" Not doubting that Mr. Dougherty had obtained good results, I asked myself a similar question soon after reading his original paper. Zaboudsky observes that the compound is easily nitrated, and it may be suggested, pending a more decisive answer to the question, that, on this account, the carbonaceous residue, when washed with HNO₃, may lose carbon without suffering any diminution in net weight; that it may even increase in weight. Mr. Dougherty will have observed, after washing with hot dilute nitric acid, that the residue changes from black to dark brown, and that the washings reduce very appreciable amounts of permanganate.

Of course the standard combustion process has sources of error to be guarded against. It seems to me, however, that the fact of their being mentioned in some instances is proof of the high degree of accuracy which analysts demand of the process. Respecting what other every-day analytical operation do we hear (if at all) nearly so frequently of the atmospheric influence on the surface of the weighed vessel as we do in relation to the KHO absorption bulb, and what can any one tell us does this amount to in extreme cases? In research work, such as was undertaken by the American Committee in connection with the International Standards, it may be important, but in every day analyses it certainly does not survive, in an appreciable form, the ordinary precautions which are taken to minimise it. Very much the same thing can be said of the other points Mr. Dougherty names, or could

name, which are essential features of the combustion process.

The results Mr. Dougherty quotes towards the end of his letter cannot be taken, and were surely never intended, to indicate the degree of error inherent in the combustion process. If they are to be discussed, without misunderstanding, then we must be assured that accidental errors and irregularities in the sample which your correspondent says "are bound to occur occasionally" have been *certainly* eliminated. This point must be the more strongly insisted on as the sample appears to have been a pig-iron containing graphite, and in that case accurate sampling from a heap of drillings is purely fortuitous. Moreover, the combined carbon, being determined by subtracting the graphite from the total carbon, shows all errors, due to more or less of the powdery graphite being taken with the sample, in the percentage of combined carbon.

With samples identical in composition such results (varying from 0.29 to 0.91 per cent) *could not* be obtained. There is the less hesitation in this statement because, during the past few years, I have personally made over five thousand such combustions, and, no matter what foreign element happened to exist in the steel, I have found the process worthy of every confidence.—I am, &c.,

HARRY BREARLEY.

Totley, near Sheffield.

THE NEWLY-DISCOVERED GASES.

To the Editor of the Chemical News.

SIR,—In a note of mine on Argon, dated March 15th, 1895, in the CHEMICAL NEWS (vol. lxxi., p. 140), an endeavour was made to show that the four metalloid series in the periodic system point to the existence of four elements of no valency of atomic weights, 20, 37, 82, and 129 respectively.

It was further remarked that the metal series also point just as strongly to the same four inactive elements in addition to others, amongst which is one of atomic weight 5.

In this connection it may be worth while to note that in an Address on "The Newly-discovered Gases" to the conference of German men of science at Munich in September last, Dr. Ramsay gave the atomic weights of the newly-discovered gases as follows (see *Nature*, vol. lxi., p. 62), viz:—

Helium	4
Neon	20
Argon	40
Krypton	82
Xenon	128

If the two sets of values are placed side by side, as in the following table, the facts speak for themselves:—

Calculated values	5	20	37	82	129
Observed values	4	20	40	82	128

—I am, &c.,

W. SEDGWICK, Lt.-Col., late R.E.

November 28, 1899.

TESTING OIL OF TURPENTINE.

To the Editor of the Chemical News.

SIR,—In commerce oil of turpentine is often replaced by "turpentine substitute," i.e., benzine, or a mixture of benzine, petroleum oil, and turpentine. An easy method of detecting the benzene, or other substances having a lower boiling-point than turpentine, is by the use of the tube described as follows:—

A piece of $\frac{1}{8}$ inch bore glass tubing 8 inches long has a bulb blown on one end; about 4 inches from this and in the length of the tube another bulb is blown; the tube between the bulbs is then heated and bent until the bulbs are opposite each other; we thus obtain a tube with a

short closed leg and a longer open leg. The turpentine to be tested is poured into the tube, and by a bit of manipulation the closed end of the tube can be completely filled; mercury is then poured into the tube, and by carefully working the matter the mercury can be made to partially fill the bulb on the closed end of the tube, and retain a small quantity of the liquid without an air bubble being present; mercury is then poured in until the level in the open leg of the tube is nearly equal to that in the closed leg. The tube is now placed in an oil-bath and heated; if the turpentine is pure there will be no motion of the mercury until a temperature of 156° C. is reached, but if benzine be present the mercury will rise in the longer leg of the tube when the temperature reaches about 148° C. In fact, if the turpentine contains any substance with a boiling-point lower than that of pure turpentine, it will be shown by the mercury being set in motion before a temperature of 156° C. is reached.—I am, &c.,

W. A. BRADBURY.

LABORATORY LAMP.

To the Editor of the Chemical News.

SIR,—“Chemicus” asks in your last issue for a lamp which will take the place of a Bunsen burner in laboratories where coal-gas is not obtainable. In one of the council's laboratories we have recently had to meet this requirement, and have obtained from the apparatus sellers a Bunsen burner, which is fed with methylated spirit from a reservoir at higher level. The spirit is converted into vapour in the lower part of the burner by the heated metal of the burner itself, and becomes mixed with air automatically in the usual way. The flame which is produced by burning this mixture is easily regulated, and is preferred to the coal-gas flame by those who are working with it. It is cleanly, hot, and inexpensive.—I am, &c.,

FRANK CLOWES.

Adsorption Test of Cadmium in presence of Copper.—Trey (*Zeit. Anal. Chemie*, xxxvii., 743). The solution received the addition of ammonia until it showed the blue colouration (presumably to re-solution of the light bluish precipitate). A drop of this solution was then allowed to wet the centre of a disc of filter-paper. In extending by capillary action Cd salt will extend outside of the part wetted by the Cu (adsorption) and testing with $(\text{NH}_4)_2\text{S}$ shows a yellow ring surrounding the brown spot due to CuS. The author devised a simple apparatus for making these tests consisting of a piece of ordinary tubing bent in U form with one end expanded to funnel shape, the other end drawn down to a fine jet, the whole set in a large flat cork, with a small wire frame to support the filter-paper which is to be laid over the jet.—*School of Mines Quarterly*.

Determining Alkaline Earths in presence of one another without previous Separation.—Knobloch (*Zeit. Anal. Chem.*, xxxvii., 734).—After qualitative tests to determine whether one, two, or all three (Ca, Sr, Ba) are present, the earths are precipitated as carbonates, and weighed as such. The filter-paper being ignited separately, and the whole treated with $(\text{NH}_4)_2\text{CO}_3$ and heated carefully at a temperature insufficient to causticise (below red heat). Then about 8 grms. of strictly C.P. borax is heated in a platinum crucible at the full heat of a Bunsen burner for two hours, cooled, and weighed. To this is then added the alkaline earth carbonates, and heat is applied carefully at first until the effervescence of CO_2 has practically ceased, when a strong heat is applied for an hour, the crucible being surrounded by a clay chimney. After cooling, the increase in weight is due to the oxides. Knowing the weight as carbonates and as oxides, the respective amounts can be calculated easily when but two are present. In case all three are present, the Ba is separated out by K_2CrO_4 in a solution slightly acid with acetic.—*School of Mines Quarterly*.

NOTICES OF BOOKS.

Tables for Quantitative Metallurgical Analysis for Laboratory Use. By J. JAMES MORGAN, F.C.S. London: C. Griffin and Co. 1899. 16 tables.

THE information given in this book will considerably lighten the labours of the metallurgical chemist, inasmuch as a large amount of detail work has been concentrated and tabulated in the familiar and useful form of analytical tables. The method of division into groups has been adopted as far as possible, and a method of analysing one member, printed in large type, is described, which, with modifications, can be easily applied to other members of the same group. The whole is admirably arranged, but we must take exception to the binding; each sheet appears to be glued to a backing, and though the book opens flat at any place it speedily comes to pieces.

Science Data Diary. Philip Harris and Co., Birmingham. 1899.

THIS handy little pocket-book contains, in a very compact form, a large number of tables, &c., of use to the chemist, engineer, and electrician. If there is a fault to be found it is that some sheets are printed in such small type as to be almost illegible.

There is also a renewable calendar and diary with lead pencil attached, making the whole a convenient little pocket-book.

Aids to the Analysis of Foods and Drugs. By T. H. PEARMAIN and C. G. MOOR, M.A., F.C.S. Second edition. London: Baillière, Tindall, and Cox. Pp. 206.

IN this, the second edition, the authors have endeavoured to bring their handy little work as much up to date as possible; a considerable amount of the most recent information has been added, while many of the articles have been entirely re-written; the portion, however, dealing with drugs has been somewhat curtailed, as this subject is more thoroughly dealt with in their larger work on "The Analysis of Foods and Drugs."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 19, November 6, 1899.

Researches on Diamines. Diethylene Diamine (Piperazine).—M. Berthelot.—Diethylene diamine is an interesting base both practically and theoretically. It is used in therapeutics under the name of spermine and piperazine. It was at first confused with the body of half its molecular weight, vinylamine and acetylamine. The author investigates this substance thermo-chemically, using for his experiments a product of which the analysis corresponds to the formula $C_4H_6N_2 \cdot 6H_2O$. He first determines the heat of dissolution of the product of distillation, a determination which tends to establish the existence of a definite hydrate.

Some of the Characteristics of Diamines.—M. Berthelot.—This paper contains an account of the behaviour of diamine in presence of colouring matters.

Preparation and Estimation of Glycogene.—Armand Gautier.—The raw material from which the glycogene is to be extracted is roughly divided—when it is not a liquid—and thrown into one and a-half times its weight of boiling water. After filtration the pulp is again boiled with water, two or three litres of water being sufficient to extract 500

grms. of muscle. The tenth part of the liquor is titrated with neutral mercury acetate, to which a little acetate of potassium has been added. From this the amount of acetate solution required to precipitate the whole can be found. The filtrate contains the glycogene.

Rhamninose.—Charles and Georges Tanret.—Rhamninose is prepared by the hydrolysis of xanthorhamnine by very dilute sulphuric acid, by which process a mixture of rhamnose, galactose, and rhamninose is obtained. The pure rhamninose is then separated, and analysis and a study of its principal reactions assign to it the formula $C_{18}H_{32}O_{14}$. It is soluble in water and alcohol, but insoluble in acetone and acetic ether.

MEETINGS FOR THE WEEK.

- MONDAY, 4th.—Royal Institution, 5. General Monthly Meeting.
Society of Chemical Industry, 8. "The Fire-proofing and Preserving of Timber," by Sherard Cowper-Coles, Assoc. M.I.C.E., &c.
Society of Arts, 8. (Cantor Lectures). "Enamelling upon Metals," by Henry Hardinge Cunynghame.
- WEDNESDAY, 6th.—Society of Arts, 8. "Artificial Silk," by Joseph Cash.
Society of Public Analysts, 8. "Note on Asa-fœtida," by C. G. Moor, M.A., F.I.C. "On some Analyses of Modern Dry Champagne," by P. Schridrowitz, Ph.D., and Otto Rosenheim, Ph.D. "On the Determination of the Iodine Value," by Dr. J. J. A. Wijs. "Treacle or Golden Syrup," by E. W. T. Jones, F.I.C. "On a Method for Distinguishing between Hops and Quassia," by A. C. Chapman, F.I.C.
- THURSDAY, 7th.—Chemical, 8. Ballot for the Election of Fellows. "The Oxidation of certain Organic Acids in presence of Iron," by H. J. H. Fenton, M.A., and H. O. Jones, B.A., B.Sc. "Determination of the Constitution of Fatty Acids" (Part II.), by A. W. Crossley, M.Sc., Ph.D., and H. R. LeSueur, B.Sc. "On Sulphates of the Form $R'_2SO_4 \cdot 2M''SO_4$, especially those of Isometric Crystallisation," by F. R. Mallet.
- FRIDAY, 8th.—Physical, 5. (At the City and Guilds Technical College, Finsbury). "Cylindrical Lenses," by Prof. Silvanus Thompson, F.R.S. "Exact Formulæ for Lenses," by T. H. Blakesley. "On an Organic Compound of great Double Refraction," by Prof. Silvanus Thompson, F.R.S.

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THE CHEMICAL NEWS.

VOL. LXXX., No. 2089.

RADIO-ACTIVITY DUE TO BECQUEREL RAYS.

By P. CURIE and Mdme. P. CURIE.

WHILST investigating the properties of the strongly radio-active materials, polonium and radium, we have found that the rays emitted by these substances, when in contact with inactive bodies, have the power of communicating their radio-activity, and that this induced radio-activity persists for a considerable time.

The radio-active material is powdered and placed on a horizontal plate; above this is placed, a few millimetres distant, the material to be tested supported on props. From time to time the upper plate is lifted, and taken immediately into the apparatus for electrical measurements, and its radio-activity determined by the conductivity which it communicates to air.

We have proved by this means the fact that the exposed plate has acquired a radio-activity, which increases with the time of exposure. At the end of some hours, however, this increase takes place very slowly, and the induced radio-activity seems to tend towards a limit. The induced radio-activity lasts for several days, but decreases, at first very rapidly, then less and less, and seems to be disappearing according to an asymptotic law.

In order to observe this phenomenon it is necessary to use substances strongly radio-active. Our experiments were performed with substances 5,000 to 50,000 times more active than uranium. The induced activity, observed immediately after exposure, varies between one and fifty times that of uranium, but was reduced to a tenth of its original value two or three hours later.

We have examined by this means the effect of Becquerel's rays on various substances—zinc, aluminium, brass, lead, platinum, bismuth, nickel, paper, barium carbonate, and bismuth sulphide. We were surprised not to find differences in the induced radio-activity in these different substances.

The aim of the present research was to find whether induced radio-activity is due to traces of the radio-active matter, which are carried in form of vapour or powder on to the exposed surface.

The analogous behaviour of the substances tried seems to point to this supposition. However, we believe that we have proved this theory to be incorrect, and that there does exist induced radio-activity. The gradual and regular disappearance of the induced activity, when the exposed plate is left in repose, seems to exclude the hypothesis of non-volatile powder, and it also would be difficult to conceive of the radiferous salts of barium being volatile. By washing the plates with water the radio-activity does not disappear, which would scarcely be the case were the activity due to a soluble powder.

Finally, we have devised with the greatest possible care an experiment which seems to us decisive. A very strongly radio-active substance (50,000 times more so than uranium) was enclosed in a metallic box, of which the bottom is formed of very thin aluminium. Plates in contact with the bottom of the box are rendered radio-active, the activity induced being ten to seventeen times greater than uranium. We obtain intense radio-active results by placing the substance to be impressed directly on the inducing substance. The phenomenon of induced radio-activity is a kind of secondary radiation due to Becquerel's rays, differing, however, from the phenomenon which is known to exist for Röntgen rays.

Indeed the secondary phenomena of Röntgen rays, as known at present, are given rise to at the moment when the body which emits them is struck by the Röntgen rays, and cease abruptly with the suppression of the latter.—*Comptes Rendus*, cxxix., No. 19, 1899.

THE SPECTRUM OF RADIUM.

By EUG. DEMARCAV.

I HAVE received during the present year several specimens of barium chloride from M. and Mdme. Curie containing radium in increasing proportion. Relatively to the increase of radiant power, the new lines show themselves more and more strongly, and further new lines have appeared, confirming the supposition that this spectrum is due to the radiant substance. In the first specimen I obtained, the radiant power was 7×10^4 times as great as that of uranium. The photographic spectrum contained lines comprised between $\lambda = 5000$ and $\lambda = 3500$. In this spectrum was noticed—

1. The spectrum of barium, very intense and complete.
2. That of the platinum electrodes and impurities—such as calcium, lead, &c.—being very weak, and reduced to their principal lines.

It contains a series of new lines, amongst which are several as strong as the strongest barium lines. These lines are as follows (the strongest intensity being marked 16, the weakest 1):—

λ .	Intensity.	λ .	Intensity.
4826.3	10	4533.5	9
4726.9	5	4458.0	3
4699.8	3	4436.1	8
4692.1	7	4364.2	3
4683.0	14	4340.6	12
4641.9	4	3814.7	16
4627.4	4	3649.6	12
4600.3	3		

$\lambda = 4627.4$ is the centre of a very characteristic symmetric nebulous band. The line marked $\lambda 4558.0$ is the same, only much weaker. All the lines are clear and sharp, and resemble those of barium in their appearance. It might be advisable to add to this list about ten other feebler lines; however, their faintness renders their origin uncertain. I believe it to be best to wait to publish these until radium has been obtained in a higher state of purity.

Finally, I may remark that, in the preceding list of the radium lines, those lines are missing which might be confounded with the eliminated lines of barium. I have also examined the less refrangible portion of this spectrum, and hope to be able to publish the results shortly.—*Comptes Rendus*, cxxix., No. 19.

THE DECOMPOSITION OF CARBONIC OXIDE IN THE PRESENCE OF METALLIC OXIDES.

By O. BOUDOUARD.

I HAVE already published the results I obtained in my research on the decomposition of carbonic oxide in the presence of metallic oxides at temperatures of 445° and 650° (*Bull. Soc. Chim.*, Series 3, vol. xxi., pp. 269 and 463). I have now continued these researches to 800° . I was, however, obliged to modify the apparatus used in the former experiments, and replace the glass tube by one of porcelain.

I used a porcelain tube glazed inside and out, 400 m.m. long, 30 m.m. outside diameter, and 24 m.m. inside diameter. This tube is connected with a capillary one,

also of porcelain, 200 m.m. long, 9 m.m. outside diameter, and 1 m.m. inside diameter. The end of this capillary tube is connected with a three-way tap, so that connection may be made with a mercury pump, or with the outside air.

The wide part of the tube is filled for a distance of about 100 m.m. with pumice containing cobalt, nickel, or iron oxides, which has already been submitted to the action of carbonic oxide at a temperature of 445° , and is covered with carbon resulting from the decomposition of the carbonic oxide. The remainder of the tube is filled with fragments of porcelain, and closed with a metal plug, cemented in, and fitted with a tap. It is from this side that the gas to be experimented on is admitted.

The apparatus thus fitted up is placed in a Mermet furnace in such a way that the part of the tube containing the pumice is directly exposed to the action of heat; the temperature is regulated by means of a Le Chatelier thermo-electric couple. The tube is filled with carbonic oxide, the two taps are closed, and the heat applied. After some time the gas is extracted by means of the pump, the apparatus being still hot; the capillary tube assists the immediate cooling of the gaseous mixture. The analysis made corresponds exactly with the condition of the mixture such as it really exists, for at the moment of extraction all contact between the gases and the carbon is instantly stopped.

The results obtained are as follows:—

Time. H. M.	Oxide of cobalt.		Oxide of nickel.		Oxide of iron.	
	CO ₂ .	CO.	CO ₂ .	CO.	CO ₂ .	CO.
0 8	4.4	95.6	3.0	97.0	3.2	96.8
0 30	5.5	94.5	4.8	95.2	—	—
0 45	5.6	94.4	—	—	—	—
2 15	7.0	93.0	6.3	93.7	—	—
4 0	6.5	93.5	6.7	93.3	—	—

The reaction of the decomposition of the carbonic oxide is thus affected by time. The quantity of carbonic acid formed increases in a regular manner, but as at 650° the decomposition of the carbonic oxide is limited. The experiments show that the reaction stops when the gaseous mixture contains 7 per cent of CO₂ and 93 per cent of CO.

It should further be noted that the speed of the reaction is much greater at 800° than at 650° ; while at 650° it was necessary to heat for six hours to attain the limit, two hours sufficed at 800° .—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 15.

ON THE EXPLOSIVE PROPERTIES OF CHLORATE OF POTASH.

By C. A. LOBRY DE BRUYN.

THE recent terrible explosion of 156 tons of chlorate of potash has not yet been forgotten. In this case the chlorate was properly packed and stored, and there was no organic matter present.

Every explosive substance should properly explode exothermically, with disengagement of gas. Chlorate of potash fulfils this condition, since, according to Berthelot, the decomposition takes place according to the following formula:—



at the same time giving off 11,000 calories.

In 1891, during a research on *bellite* (4 parts of nitrate of ammonium to 1 part of dinitrobenzene) I showed that while *bellite* could be exploded by means of an ordinary detonator containing 1 grm. of fulminate of mercury, nitrate of ammonium requires, on the contrary, a much more powerful detonator. In this case there must be used

at least 3 grms. of fulminate of mercury, or 10 to 30 grms. of *bellite*, itself acting as a fulminate.

The disaster at St. Helens appears to me to be analogous to a local fire which broke out in a gun-cotton magazine; the fire began slowly, the gun-cotton simply decomposed and burnt. After this the fire spread, and eventually a moment occurred when the gas generated could not escape sufficiently quickly; thus it collected and acted the part of a detonator and caused the remainder of the gun-cotton to explode with violence.

As a matter of fact chlorate of potash requires a much more powerful detonator than does gun-cotton; it is not combustible by itself, but it is probable that at St. Helens a portion of the salt was decomposed by a local fire in the immediate neighbourhood of the magazine, and that the rapid accumulation of gas caused the explosion above referred to.—*Zeitschr. f. Angewandte Chemie*, 1899, [27], p. 633.

A METHOD FOR THE DETERMINATION OF THE MELTING-POINT.

By M. KUHARA, Ph.D., and M. CHIKASHIGÉ, B.Sc.

SEVERAL different methods have hitherto been suggested for determining the melting-point of substances; one of which, that now in common use, consists in heating the substance to be experimented upon in a capillary tube, fastened to a thermometer, and immersed in a bath. It is usual, in this case, to take as its melting-point the temperature at which the substance begins to melt away from the walls of the capillary tube. This method, however, is very liable to give too high results, as it is a hard task to observe the exact point of fusion of that portion of the substance which is in contact with the walls of the tube, before the inner portion thereof reaches its melting-point: this is apparently higher than the real melting-point, owing to the bad conductivity of the air contained in the interstices of the substance and the consequent over-heating. We also find another disadvantage in this method, namely, that substances which cannot be pulverised—such as waxes, fats, &c.—are with difficulty introduced into the capillary tube.

We have recently devised a method which, we think, will eliminate all the disadvantages of the tube-method, and which, moreover, can easily be carried on in chemical laboratories.

In this new method, instead of a capillary tube, we make use of a pair of cover-glasses for microscopical purposes, cut in halves, between which the substance to be tested is introduced, either in powder, in crystals, or in thin slices. If the substance be in the state of powder, we can make the layer as thin as possible by pressing and sliding the two pieces with the fingers, so that the heat of the bath may at once be conducted throughout the whole mass. The surface exposed is very large compared with the quantity of the substance taken, and, consequently, its behaviour towards heat may be distinctly observed. Before the substance is melted the glass appears opaque, while it becomes transparent when fusion occurs. The thinner the layer the more distinct is the demarcation; but with volatile substances a quantity somewhat in excess of what is apparently essential should be taken, in order to make allowance for loss by volatilisation.

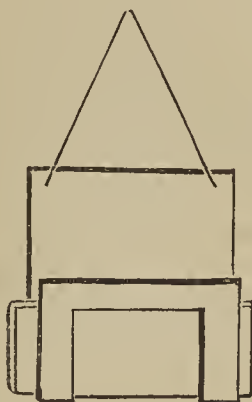
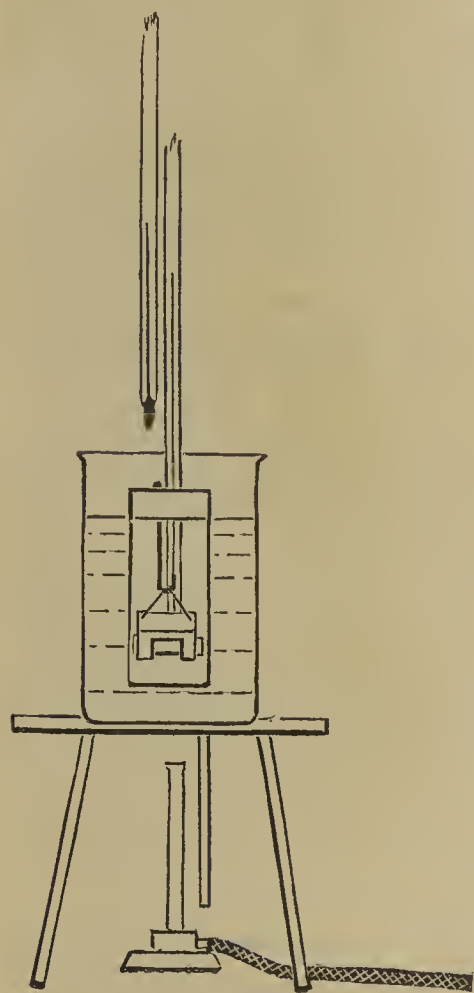
The pair of glass-pieces is then fastened to a holder made of platinum-foil, and tied, if necessary, with a piece of fine wire of the same material. The holder, which can easily be made by folding the foil and cutting it with scissors, as shown in the annexed figure, is suspended in a wide test-tube into which is inserted a thermometer close to the holder. The test-tube, serving as an air-bath, is immersed in the sulphuric acid bath almost to its mouth. The further steps of the process require no modification of the old methods.

The glass-pieces can be used any number of times, unless they are broken; this is considered another superiority over the tube-method.

The result of experiments with our method is given in the following table. The substances taken were purified by repeated crystallisation, and the temperatures given are the corrected ones:—

Substance.	I.	II.	III.	Mean.	M.-p. already known.	Observer.
Chloral hydrate	57'3	57'3	57'0	57'2	57	Meyer & Dulk.
Urea	132'1	132'1	132'3	132'2	132	Lubavin.
Phthalic acid..	203'2	202'7	203'0	203'0	203	Ador.
Phthalimide ..	233'6	233'7	233'6	233'6	233'5	Graebe.

The melting-point of phthalic acid has been a subject of discussion, the figures differing considerably in every case of determination. Lossen (*Annalen*, cxliv., 76) gives it as low as 184°, but Ador (*Annalen*, clxiii., 230) states that crystallised phthalic acid melts at 213°, and the pow-



dered substance at 203°. Remsen (*Amer. Chem. Journ.*, viii., 30) ascribes the cause of such variation to the fact that phthalic anhydride, formed partly from the acid, lowers the melting-point of the mixture. In order to verify his view, small quantities of the acid, introduced into a U-tube, were heated over a paraffin bath at the temperatures of 140° and 170°, and the melting-point was found to be considerably lowered in both cases. This experiment was conducted by one of us a number of years ago, when working in his laboratory. We have found, however, with the new method, that both the crystallised and the powdered substances melt equally at the constant temperature of 203°, whether the air-tube be gradually heated or plunged at once into the bath at a temperature above 205°. This may probably be due to the fact that the anhydride formed is freely volatilised in our apparatus through the interstice of the two glass-pieces, and the remaining acid, kept pure, melts at its proper temperature. With our method we have never observed a temperature so high as 213° nor so low as 184°, while with the capillary-tube method we often noted a melting-point as low as 185°.

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A BIBLIOGRAPHY OF STEEL-WORKS ANALYSIS.

By HARRY BREARLEY.

(Concluded from p. 258).

MANGANESE: IV. VOLUMETRIC ESTIMATION OF MANGANESE (*continued*).

IVc. Oxidation to Higher Oxides of Mn.

IV.c. i. The Chlorate Process.—

143. HANNAY (C. N., xxxvi., 212).—MnO₂ precipitated by heating with HNO₃ and KClO₃. In presence of Fe a double manganate of Fe and Mn is precipitated. Refers to the process as a means of separating Fe and Al.
144. STORER (C. N., xxi., 195).—Oxidising value of HNO₃ and KClO₃ applied to assays of S and Cr compounds, &c.
145. WILLIAMS (J. I. S. I., 1881, 656).—Filter MnO₂ from the strong acid solution. Titrate with oxalic acid and permanganate.
146. MEINECKE (J. C. S., lii., 531).—In the presence of Fe, warm dilute HNO₃ dissolves a little MnO₂ as precipitated by the KClO₃ process.
147. JULIAN (C. N., lviii., 209; and J. I. S. I., 1888, i., 376).—The precipitated solution is diluted, excess oxalic acid added, and titration with KMnO₄ speedily made. KMnO₄ standardised by adding oxalic acid to nitric solution from which MnO₂ has been filtered.
148. STONE (J. I. S. I., 1883, 366).—The Mn precipitated with KClO₃ approximates to 10MnO₂.MnO, and therefore oxidimetric estimations give low results. The standard solutions should be standardised with a spiegel of known composition. . . Separation with acetate and estimation as Mn₂P₂O₇ most accurate gravimetric process.
149. RAYMOND, TROILIUS, and MACKINTOSH (J. I. S. I., 1883, 783).—MnO₂ dissolved in FeSO₄ and titrated. That the precipitate is not MnO₂ strongly repudiated; necessary to divide KClO₃ into small portions, and add alternately with strong HNO₃ in order to secure MnO₂. (See also MACKINTOSH, C. N., xlviii., 176).
150. STONE (C. N., xlviii., 273).—Defends his previous statement (see 148). The MnO₂ may be filtered from the hot as well as from the cold solution.
151. MACKINTOSH (C. N., i., 75).—Influence of organic matter and iron on the process. Results a trifle low. Low results may sometimes be due to KCl in the KClO₃ giving rise to free HCl.
152. TROILIUS (J. C. S., xlviii., 597).—The presence of Fe(NO₃)₃ facilitates precipitation with KClO₃. Lead, Cu, Ni, and Co are precipitated with the MnO₂, and give high results.
153. RAYMOND (C. N., xlviii., 23).—After precipitating MnO₂, the solution is diluted with hot water before filtering.
154. J. T. (C. N., lxxix., 157).—Cr steels are incompletely soluble in HNO₃, hence the chlorate process is open to error by the unattacked metal being soluble in the acid solution of FeSO₄ used in titrating.
155. HAMPE (J. I. S. I., 1885, 652).—Gives equations representing the changes. Neither HCl nor H₂SO₄ should be present, nor should large amounts of H₃PO₄ (see 158). The MnO₂ always contains foreign metals if such are in solution; Ni, Cu, Zn, and Sn are without influence; Co, Pb, and Bi cause high results; all such errors are eliminated by re-precipitating. KClO₃ should be added, little by little, so long as green vapours are evolved, boiled five or ten minutes, and filtered. Precipitate should be washed with water; HNO₃ unnecessary and may contain nitrous acid.

156. CHEEVER (*J. I. S. I.*, 1885, 736).—Strong HNO_3 is added finally, and boiled to completely decompose KClO_3 . Precipitate must be washed with nitrous-free HNO_3 ; if washed with water Mn would be dissolved.
157. REIS (*J. C. S.*, lxii., 1132).—Modified process: use weaker acid and add KClO_3 all at once. Hampe (*ibid.*) strongly protests against these modifications.
158. VIARD (*J. C. S.*, lxxii., ii., 519).—Process inapplicable in the presence of phosphoric acid, owing to the formation of trimanganic phosphate (see 132).
159. GOOCH and AUSTIN (*C. N.*, lxxvii., 269).—Short historical account of the process, possibility of KClO_3 being mechanically occluded in the MnO_2 . Soda chlorate more soluble and more easily decomposed; precipitation complete if solution is just raised to boiling after final addition of NaClO_3 ; prolonged boiling leads to loss, probably due to solvent action of lower oxides of N in absence of Cl, dilution before filtration tends to dissolve Mn; oxidimetric estimation with arsenious acid and iodine; the precipitate not MnO_2 , error may be 2 per cent or more if taken as such; solution of MnO_2 , and precipitation at 80°C . with excess of permanganate in presence of ZnSO_4 , throws down true MnO_2 .
160. REINHARDT (*J. I. S. I.*, 1888, i., 377).— KClO_3 process not suitable for irons poor in Mn, and rich in Si. Describes a process similar to 171.
161. NORRIS (*C. N.*, lxiv., 242).—Process applied to slags by treating with HNO_3 and adding HF, boiling off excess HF and adding KClO_3 . For ores, solution is effected with HNO_3 , tartaric acid, and HF.
162. FORD and BREGOWSKY (*J. C. S.*, lxxiv., ii., 540).— SiO_2 is decomposed with a few drops of HF. The Mn, especially in ores, is more completely precipitated when HF has been used.
163. JEAN (*J. C. S.*, lxiv., ii., 498).—Decomposes minerals with HCl, precipitates with soda carbonate, dissolves in HNO_3 , and precipitates Mn with KClO_3 .
- IV.c. 2. Other Oxidimetric Processes.—
164. PARRY (*C. N.*, xxix., 86).—Dissolve spiegel in HNO_3 , evaporate, and heat to redness over Bunsen; cool, add sodium oxalate and HCl; heat, and collect CO_2 in graduated tube.
165. GALBRAITH (*C. N.*, xxxiii., 47).—Proceeds like Parry, but adds FeSO_4 and HCl and heats; the FeSO_4 unoxidised by the Cl is titrated (see 196).
166. CARNOT (*C. N.*, lxviii., 51).—Evaporation of an HNO_3 solution to dryness, and ignition of the residue, yields an oxide remote from MnO_2 . Repeated ignition below 200°C . improves matters, but the practice is uncertain.
167. MEINECKE (*J. C. S.*, lii., 1139).—Precipitate Fe and Mn together with HgO and Br water. The MnO_2 is determined with oxalic acid and KMnO_4 .
168. REINHARDT (*C. N.*, lviii., 173).—Mn precipitated with sodium acetate, Br, and ZnO ; and MnO_2 titrated with oxalic acid and KMnO_4 .
169. LOW (*C. N.*, lxvii., 162).—Precipitation with ZnO and Br, and titration as above; ordinary constituents of ores do not interfere.
170. VORTMANN (*C. N.*, lxii., 251).—Alum, iodine solution, and NaHO are used to precipitate MnO solution. Iodine determined in filtrate with thio-sulphate. Alum ensures formation of MnO_2 . Process available in presence of Fe and Al.
171. REINHARDT (*J. I. S. I.*, 1886, 393).—Fe precipitated with acetate and partly removed; Mn precipitated with Br and ammonia; MnO_2 titrated with FeSO_4 , &c. This is spoken of as the Belani method. Meinecke's process of titrating is to add an excess of $\text{KMnO}_4 + \text{ZnSO}_4$, and determine excess KMnO_4 with antimony chloride. Muller (*J. I. S. I.*, 1886, 1022) recommends Meinecke's process, especially for highly manganiferous alloys.
172. ROSENTHAL (*C. N.*, xxxvi., 147).—Precipitates as $\text{MnO}_2 \cdot \text{H}_2\text{O}$ with H_2O_2 and ammonia. Large excess of H_2O_2 should be avoided; much $(\text{NH}_4)\text{Cl}$ is objectionable.
173. BARLOW (*C. N.*, liii., 41).—Precipitates as above; precipitate completely insoluble in ammonia salts, and quite free from Ni, Co, or Zn. In presence of Fe the ignited $\text{Fe}_2\text{O}_3 + \text{Mn}_2\text{O}_3$ is distilled with HCl, the Cl being absorbed in KI, &c. (see 201).
174. CARNOT (*C. N.*, lix., 16).—Precipitates entirely as MnO_2 with H_2O_2 and ammonia. Estimated with oxalic acid and permanganate.
175. MCCULLOCH (*C. N.*, lix., 35).—Contends that Mn as precipitated by Carnot has varying composition, but approximately is Mn_7O_{13} Carnot later (*C. N.*, lix., 48) says the Mn is precipitated as $5\text{MnO}_2 \cdot \text{MnO}$ (Mn_6O_{11}).
176. CARNOT (*J. I. S. I.*, 1893, ii., 531; 1895, i., 507).—Precipitate with H_2O_2 , large amounts of NH_3 salts give low results. Zn, Cu, Ni, and Co form complex salts ($\text{ZnO}_5 \cdot \text{MnO}_2$), but are eliminated by re-precipitating. Fe causes no inconvenience if below 60 per cent; if more, preliminary separation with KClO_3 . (*C. N.*, lxviii., 51).—Influence of HN_3 salts overcome by large amounts of H_2O_2 . Mn may also be precipitated with Br and $(\text{NH}_4)\text{HO}$ in the cold as Mn_6O_{11} .
177. ULZER and BRUHL (*J. I. S. I.*, 1896, ii., 442).—Precipitate with H_2O_2 and NaHO . Titrate with oxalic and KMnO_4 .
178. PATTINSON (*C. N.*, xxxix., 201).—Precipitated by hypochlorite or bromine and CaCO_3 in presence of ZnCl_2 or Fe_2Cl_6 , dissolved in FeSO_4 , and excess titrated with $\text{K}_2\text{Cr}_2\text{O}_7$ (see 213).
179. LUNGE (*C. N.*, xli., 141).—That Ca salts have the same rôle as Zn salts in Pattinson's process. Processes for the analysis of Weldon mud discussed.
180. WELDON (*C. N.*, xli., 207).—Finds merely boiling slightly acidified MnCl_2 with enough bleaching-powder to produce a faint KMnO_4 colour to give results comparing with Pattinson's process, as 100:100.26.
181. ATKINSON (*J. C. S.*, lii., 399).—Pattinson's process gives slightly low results, due to incomplete oxidation of the Mn.
182. ROSSI (*J. I. S. I.*, 1891, i., 443).—Good account of Pattinson's process applied to manganiferous iron ores.
183. MITTENZWEY (*C. N.*, ix., 253).— MnO solution made alkaline and shaken in a closed vessel. Amount of water needed to fill the partial vacuum equals amount of oxygen absorbed; calculation empirical; reaction certainly not so far as MnO_2 (see 76). Other bodies similarly estimated.
184. SCHMID (*C. N.*, xiv., 107).—Freshly precipitated MnO_2 precipitates CuO_2 from CuSO_4 . $\text{CuO} = \text{MnO}_2$ quantitatively true.
185. CARNOT (*C. N.*, lxviii., 51).—Oxalic acid and KMnO_4 are the best reagents for oxidimetric estimations.
186. KALMAN and SMOLKA (*C. N.*, li., 230; *J. I. S. I.*, 1885, 248).—Fuse with borax and alkaline carbonate, dissolve in FeSO_4 , and titrate with permanganate. Suitable whenever the sample can be heated to Mn_3O_4 .
187. MYHLERTZ (*J. C. S.*, lx., 366).—Fuse with sodium carbonate and KNO_3 , digest with H_2O , reduce with alcohol; MnO_2 determined with FeSO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$.
188. ALT (*J. C. S.*, lviii., 419).—By aspirating Br fumes through a previously boiled MnO solution containing $(\text{NH}_4)\text{Cl}$ and NH_3 , MnO_2 is precipitated without staining the sides of the flask.

IV.c. 3. Available Oxygen in Ores, &c.—

189. SHERER and RUMPF (*C. N.*, xx., 302; and xxi., 48).—Comparison of Fresenius and Will's, iron, chloride of lime, and Bunsen methods.
190. PATTINSON (*C. N.*, xxi., 267).—The high percentage of available oxygen given by Fresenius and Will's process is not generally due to FeO. Describes a modified iron method.
191. PAUL (*C. N.*, xxi., 16).—Dissolve ore along with oxalic acid in H_2SO_4 ; titrated with permanganate.
192. HARVEY (*C. N.*, xlvii., 2).—Heats with $SnCl_2$ and HCl, and estimates excess $SnCl_2$ with Fe_2Cl_6 and $K_2Cr_2O_7$.
193. CHARPENTIER (*C. N.*, lii., 86).—Pass liberated Cl into $FeSO_4$; KCNS and standard KHO added until solution is decolourised. Or Cl collected in $AgNO_3$, add drop $Fe(NO_3)_3$, and titrate with KCNS. The reaction sensitive to 1/3,000,000.
194. LUNGE (*Z. C. S.*, lviii., 1470).—Ore decomposed according to the equation—
 $MnO_2 + H_2O_2 + H_2SO_4 = MnSO_4 + 2H_2O + O_2$;
the O is measured in the nitrometer.
195. CARNOT (*C. N.*, lxviii., 15 and 301).—The oxide reacts with a nitric solution of H_2O_2 , and the evolved O is measured. JONES (*C. N.*, lxviii., 305) draws attention to previous proposals, and also to the fact that higher oxides of Pb may be similarly estimated.

IV.d. Indirect Processes of Estimating Manganese.—

196. RILEY (*C. N.*, xxxv., 175).—Dissolve in dilute H_2SO_4 ; allow 5 per cent for C, &c.; difference, Mn. Results low, owing to soluble organic matter; obviated by taking nitric acid solution to dryness, dissolving in HCl, and reducing with Na_2SO_3 . Methods of Parry and Galbraith (164 and 165) are undesirable ones.
197. HOLDICH (*C. N.*, xlix., 9).—As Riley; but recommends a subtraction of determined Si.
198. ATKINSON (*C. N.*, xlix., 25).—Subtracts Fe and Si + 6 per cent for ferro-manganese. Results not so regular as with speigels.
199. PARRY (*C. N.*, lxvii., 296).—Allows 6 per cent for spiegel and 7 per cent for ferro-manganese.
200. TROILIUS (*Z. I. S. I.*, 1883, 784).—7.5 per cent allowed for impurities if Fe is less than 20 per cent; 6.5 if Fe is 20 to 45 per cent; 6.0 per cent if Fe is 45 to 65 per cent; and 5.5 per cent for upwards of 65 per cent Fe. These are Ledebur's figures.
201. DIEHL (*Z. C. S.*, l., 101).—Mn and Fe are precipitated with Br and NH_3 ; ignited; Fe determined volumetrically, Mn by difference.

IV.e. Miscellaneous Volumetric Processes.—

202. LEISON (*C. N.*, xxii., 210).—Mn completely precipitated as oxalate; estimated by titration with permanganate. The separation of metals as oxalates is discussed by LUCKOW (*C. N.*, lv., 73).
203. BLUM (*Z. C. S.*, lx., 1293).—Boiling ammoniacal solution containing Mn, Fe, $(NH_4)Cl$, and tartaric acid is titrated with ferrocyanide; acetic acid used as indicator.
204. FRESSENIUS ("Quant. Anal.").—Adds an excess of ferricyanide, and determines the ferrocyanide formed by means of $KMnO_4$.
205. NASS (*Z. C. S.*, lxvi., 1482).—Classen's process (precipitation as oxalate) useless for estimating Mn, Co, or Ni.
206. NEUMANN (*C. N.*, lxxii., 212).—Neutral solution precipitated with alkaline sulphide; excess of sulphide estimated. Process applied to a dozen other metals.
207. RÖSSLER (*C. N.*, xl., 169).—MnO solution, free from halogens and organic matter, mixed with standard Ag solution; Ag precipitated with sodium car-

bonate; excess $(NH_4)HO$ added; filtrate titrated with KCNS. A similar process for cobalt (*C. N.*, xli., 184).

208. PURGOTTI (*Z. C. S.*, lxxii., ii., 349).— MnO_2 reacts with hydrazine sulphate to form N, which is measured at N. T. P. Per cent Mn calculated from this.

V. DETECTION OF MANGANESE.

209. BÖTTGER (*C. N.*, xxiv., 192).—Fragment of the substance dropped into fused $KClO_3$. Peach-blossom red indicates Mn.
210. HILLEBRAND (*C. N.*, lxxviii., 80).—During fusion an oxidising atmosphere must be in the crucible, otherwise negative results are obtainable when Mn is present.

VI. MISCELLANEOUS NOTES.

211. KERN (*C. N.*, xxxviii., 268).—Mn unequally distributed in alloys. A difference of 2.2 per cent observed.
212. CARNOT and GOUTAL (*Z. C. S.*, lxxii., ii., 555).—If in small quantity, Mn is present in iron as silicide or sulphide. In larger amounts, it is either partly dissolved or in combination with the iron.
213. LEDEBUR (*Z. I. S. I.*, 1884, 269).—Compares Volhard, chlorate, and Pattinson processes. In $KClO_3$ process the precipitated solution was heated near boiling-point for two hours; results 0.5 to 1.0 per cent too low; very difficult to wash free from $KClO_3$. Pattinson's process most meritorious, but Cu, Co, and Ni cause plus errors.
214. SANITER (*Z. I. S. I.*, 1894, 613).—Reviews Pattinson, Volhard, pyrophosphate, and Mn_3O_4 methods. The latter trustworthy if Mn has been precipitated as hydrated dioxide.
215. RURUP (*Z. I. S. I.*, 1896, i., 534).—Examines estimation as sulphide, Mn_3O_4 ; chlorate process (Ford's), weighing as Mn_3O_4 ; Volhard's, separation of Fe with Na_2SO_4 and titrating with $KMnO_4$; and the $KClO_3$ volumetric process. All accurate for steel works purposes.
216. JUPTNER (*Z. I. S. I.*, 1895, i., 507).—Draws attention to various atomic weight values as a cause of differences.
217. HOGG (*C. N.*, lxviii., 163).—Cyano-nitride of titanium occurs in all high-grade speigels and ferro-manganeses. In the latter, half a million separate crystals are calculated to occur in each cubic inch; they are separated by elutriating the nitric acid residue.

Spectroscopy and Spectrum Photography.—At the University College, London, a Course of Eight Lectures dealing with the methods of Spectroscopy especially in connexion with the Photography of the Spectrum will be given by Mr. E. C. C. Baly, on Friday Evenings, at 5.30 o'clock, commencing on January 19th, 1900. Fee for the course, One guinea. The following subjects will be treated and illustrated by experiments:—

The simple theory of refraction and diffraction.

The history of the determination of the modern standards of wave-lengths.

The Prism Spectroscope and its integral parts.

The comparison of spectra and determination of wave-lengths visually and photographically with Prism apparatus.

The Grating Spectroscope. Rowland's concave gratings; their mounting and adjustment.

The determination of wave-lengths with the grating.

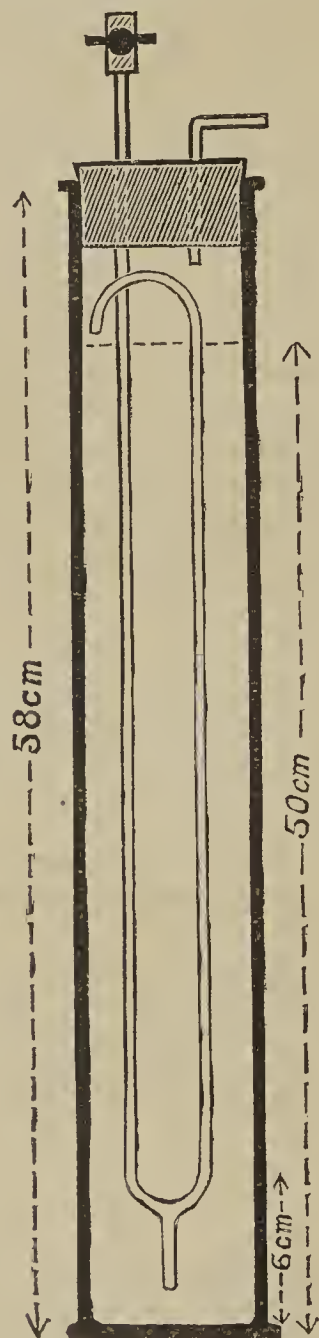
Photography of the Spectrum.

Methods of producing emission and absorption spectra. Fluorescence and Phosphorescence.

A DISSOLVER.

By ARTHUR JOHN HOPKINS.

AN apparatus for hastening the solution of salts has been described by Richards (*American Chemical Journal*, xx., 189). That such devices will supplant the good old methods of heating or stirring is not to be supposed; but heating is often proscribed by the nature of the salt or the requirement of a constant temperature, and stirring by hand is laborious and inconstant: and although both constant temperature and constant circulation are supplied by mechanical stirrers, yet it is possible that the necessity for mechanical devices has deterred many a chemist from entering upon the study of solubilities. A field may therefore be open for an apparatus serving the same purpose as a stirrer and constructed from material with which the chemist is already familiar.



Richards's dissolver, although of simple construction, is very efficient, and moreover is automatic, in that it requires no stirrer. Its efficiency is obviously limited to such salts as can form saturated solutions of much greater specific gravity than the solvent, and further limited to the formation of non-saturated solutions of these salts. The rate of flow in a purely automatic dissolver will rapidly approach zero, as the specific gravity of the solvent gains on that of the saturated solution. In fact, at any one moment the rapidity of solution varies as the square of the velocity of the solvent passing the crystals.

In the hope of making a dissolver which shall be universally applicable without resorting to mechanical stirrers, an attempt has been made in this laboratory to apply a well-known device to this problem. The result is a dissolver of simple construction and great efficiency, which will rapidly prepare solutions of any specific gravity.

The accompanying illustration shows such an apparatus. An ordinary glass cylinder of any convenient size may be used. The one represented holds 2200 c.c.* Through one hole of a two-holed stopper is passed a straight glass tube of about 6 m.m. bore, fitted at the upper end with a short rubber tube and screw-cock. The lower end of this glass tube is fused, or bound by aid of rubber connection tubing, to one arm of a Y-tube, the lower arm of which reaches nearly to the bottom of the cylinder. The third arm of the Y-tube meets a second glass tube, which reaches up nearly to the stopper, and there curves down to give direction to the concentrating solution. The second hole of the stopper carries a short exit tube bent at a right angle, the lower portion of which extends to a point just below the bottom of the stopper.

To use the dissolver, introduce the desired quantity of water or other solvent with the weighed quantity of salt to be dissolved, then put the stopper, carrying its tubes, firmly into position, and apply, by means of a filter-pump attached to the short right-angled tube, enough suction to overcome the water pressure of 44 c.m. A current of air, regulated by the screw-cock to prevent vibrations in the Y-tube, follows the water down the long tube in continuous column, but continues only as far as the junction of the Y-tube, for there it is broken into little columns alternating with columns of the saturating solution drawn up through the lower arm of the Y-tube. These broken columns of air, rising through the curved tube, lift the solution drawn directly from the crystals, and throw it out upon the least saturated solvent at the top. The air escapes through the short tube, and the fresh solvent, which occupied the upper position in the cylinder at the beginning, sinks down to dissolve more of the crystals below. When a carefully regulated and not too great suction is applied, there is a continuous and rapid current of the solution passing the crystals, while the saturated solution may be seen streaming from the crystals to the lower end of the Y-tube.

To test the efficiency of this apparatus, 30 grms. of copper sulphate, in crystals of about 2 grms. each, were dissolved in 200 c.c. of distilled water at 19°. For this purpose a cylinder of about one-tenth the size described was selected. Complete solution took place in about forty minutes.

In order to prepare a solution of ammonium carbonate for use in qualitative analysis, a very large stand-cylinder which had formerly served as a generator of hydrogen sulphide, was employed. The proper tubes were attached to the stopper, and, when 1 kilo. of commercial ammonium carbonate, 1 litre of concentrated ammonium hydroxide, and 4 litres of distilled water had been placed in the stand-glass, suction was applied, and in thirty minutes all but about 20 grms. of the salt had been dissolved. Dissolving this salt in such large quantities by the usual method takes not less than four or five consecutive hours, and in busy laboratories a day or two of intermittent stirring is often allowed. Assembling the parts of the apparatus and affecting the solution, in the case cited, required less than forty-five minutes.

This dissolver has been used, in a bath of constant temperature, for making saturated solutions of copper sulphate, and for determining the solubility of this salt at different temperatures. For this purpose the lower end of the short reduction-tube was protected, and the entering air was washed through caustic potash and then through sulphuric acid, and again washed on leaving through weighed sulphuric acid tubes. Completely saturated solutions were obtained in about ninety minutes. This work will be taken up again in this laboratory and reported upon.

The dissolver here described, like that of Richards, requires no attention, and is very easily constructed in a few minutes from ordinary laboratory material. It in-

* It is best to choose a cylinder of such size that the quantity of solution desired shall fill it to a point just below the curved tube.

volves no mechanical difficulties, is universally applicable, and seems as rapid as any of the mechanical stirrers or shakers.—*American Chemical Journal*, November, 1899, p. 407.

A NEW VOLUMETRIC METHOD FOR MAGNESIUM.*

By RICHARD K. MEADE.

ONE of the elements for which, so far, no satisfactory volumetric method of determination, of general application, has been found, is magnesium. Stolba (*Chem. Centrbl.*, 1866, 728) suggested a volumetric method depending upon the fact that 1 molecule of magnesium ammonium phosphate required 2 molecules of mineral acid for solution. Hart and Sutton both describe the method in detail, in their works upon volumetric analysis, and call attention to its accuracy. Hartzell, a student in the laboratory of Lafayette College, in his thesis work for graduation, in 1897, made use of the method in determining magnesia in cement, and the result of his investigations also showed the method to be fairly accurate. The great objection to Stolba's method, particularly if it is resorted to as a time-saver, is the tedious washing of the precipitated magnesia with alcohol, in order to get rid of the ammonia, making the volumetric determination very little, if any, quicker than the gravimetric. In any event, so far as I know, the method is very little if ever used, even in commercial laboratories where magnesia determinations are a part of the daily routine.

Analogous to the phosphates are the arsenates. If instead of adding sodium phosphate to an ammoniacal solution containing magnesium we add sodium arsenate, magnesium ammonium arsenate, corresponding to magnesium ammonium phosphate, is precipitated. This reaction is of course a familiar one, since it is the one upon which the usual gravimetric determination of arsenic is based. Now if the magnesium in a solution can be entirely precipitated as a double arsenate of magnesium and ammonium, if the magnesium and arsenic in this compound bear a fixed ratio to each other, if the precipitate can be collected and washed free from sodium arsenate, then clearly any volumetric method which will give us the weight of arsenic in the precipitate will also tell us indirectly the amount of magnesium in the solution. From the formula of the double salt, $Mg_2(NH_4)_2As_2O_8 \cdot H_2O$, it will be seen that one atom of magnesium is equivalent to one atom of arsenic, and consequently the ratio between the magnesium and arsenic is 24.28 : 75.01.

As the first step looking to the formulation of a volumetric method along these lines, a stock solution of magnesium was prepared as follows:—Fifty grms. of pure magnesium chloride were dissolved in about 700 c.c. of water, and a little ammonium oxalate added to precipitate any traces of calcium present. The solution was allowed to stand for a day, when the very slight precipitate of calcium oxalate was filtered off. A sufficient quantity of ammonium oxalate to convert all the magnesium in the solution to magnesium oxalate was next added, and the solution evaporated to small bulk over a water-bath. The separated magnesium oxalate was collected, washed, dried, and ignited, first at a low temperature, and then at a higher, until finally at a red heat. Of the pure magnesium thus obtained, 5 grms. were dissolved in dilute hydrochloric acid and the solution diluted to 2 litres. Each 50 c.c. of this solution should have been equivalent to 0.2500 gm. of magnesium oxide. Checked by precipitation with sodium phosphate, 50 c.c. gave—

I. 0.6900 gm. of $Mg_2P_2O_7$, equivalent to 0.2497 gm. of MgO.

II. 0.6891 gm. of $Mg_2P_2O_7$, equivalent to 0.2493 gm. of MgO.

* Read before the Lehigh Valley Section of the American Chemical Society, May 16, 1899. From the *Journal of the American Chemical Society*, vol. xxi., No. 9, September, 1899.

Checked by evaporation to dryness and ignition of the residue, 50 c.c. gave—

0.2490 gm. of MgO.

0.2498 gm. of MgO.

The average of the four determinations is 0.2495 gm. of MgO.

A search into the literature on the solubility of the magnesium ammonium arsenate showed the precipitate to be less soluble where an excess of sodium arsenate was present in the ammoniacal solution; accordingly, wherever the magnesium was precipitated by sodium arsenate, a considerable excess of the precipitant was used. The precipitate of course must be washed with dilute ammonia water, and, as it is not entirely insoluble in this medium, the volume of the washing fluid should be kept as small as possible.

Following these points, 50 c.c. of the stock solution were diluted to 500 c.c., and 50 c.c. of sodium arsenate (10 per cent) solution added; then ammonia, drop by drop, with constant stirring until the precipitate began to form. At this point the addition of ammonia was interrupted and the solution stirred for five minutes, after which one-sixth the volume of the solution of strong ammonia was added and the mixture stirred for five minutes longer and allowed to stand over night. In the morning the precipitated magnesium ammonium arsenate was collected in a Gooch crucible, dried, and ignited at a very low temperature, and weighed as magnesium pyroarsenate, containing 25.94 per cent of magnesium oxide. The results were:—

No.	$Mg_2As_2O_7$ Grm.	Equivalent to MgO. Grm.
1	0.9599	0.2490
2	0.9545	0.2476
3	0.9592	0.2488
4	0.9573	0.2483
Average	0.2484
Instead of	0.2495
Difference	0.0009

As a further test the magnesia from 50 c.c. of the stock solution was precipitated as described, dissolved in dilute hydrochloric acid, and the arsenic thrown out of solution with hydrogen sulphide. The magnesium remaining was then determined as pyrophosphate with the following results:—

No.	$Mg_3P_2O_7$ Grm.	Equivalent to MgO. Grm.
1	0.6883	0.2490
2	0.6865	0.2484
3	0.6870	0.2486
Average	0.2487
Instead of	0.2495
Difference	0.0008

In the same manner, the magnesium in 50 c.c. of the stock solution was precipitated as magnesium ammonium arsenate, dissolved in hydrochloric acid, and the arsenic determined as magnesium pyroarsenate by addition of magnesia mixture. The results were:—

No.	$Mg_3As_2O_7$ Grm.	Equivalent to MgO. Grm.
1	0.9590	0.2488
2	0.9536	0.2474
3	0.9552	0.2478
Average	0.2481
Instead of	0.2495
Difference	0.0014

These three sets of results, while a little low, showing that a slight loss of magnesia is incurred, probably due to solution of the precipitate in the mother-liquor and the wash-water, nevertheless fall well within the limits of allowable variation for technical work, and show the ratio between the magnesium and arsenic to be constant.

The next step was to find a suitable volumetric method for determining the arsenic. This being in the state of arsenic acid excluded all methods supposing the element to be in the condition of lower oxidation. The methods of Pierce and McCay depending upon the precipitation of the arsenic as silver arsenate by an excess of standard silver nitrate and the determination of either the silver in the precipitate or the excess of silver in the solution by titration with sodium thiocyanate, were also not considered, as both time and expense made them unsuitable for commercial work.

Of the methods depending upon the reduction of the arsenic to arsenious acid and the titration of the latter by standard iodine, that making use of the reaction between arsenic acid and potassium iodide in acid solutions, offered the best field for investigation, and, following the method as laid down by Gooch and Browning (*Am. J. Sci.*, [3], xl., 66), several determinations were made. The process followed consisted in dissolving the precipitated arsenate in dilute sulphuric acid, adding an excess of potassium iodide and 10 c.c. of sulphuric acid (1:1), and diluting to 100 c.c. The solution was boiled rapidly until the volume reached 40 c.c. and the free iodine in the solution destroyed by careful addition of sulphurous acid (roughly made about one-half normal). Sodium carbonate was then added until the solution was nearly neutral, and next an excess of sodium bicarbonate over what was required to make it so. The arsenious acid was then titrated with standard iodine solution. This latter was made by dissolving 52.24 grms. of pure re-sublimed iodine in a solution of 75 grms. of potassium iodide in 200 c.c. of water and diluting to 1 litre. Each c.c. of this solution should be equivalent to 0.005 gm. of magnesium oxide. The following satisfactory results were obtained by this method:—

No.	Stock solution taken. C.c.	Equivalent to MgO. Grm.	Iodine required. C.c.	Equivalent to MgO. Grm.
1	50	0.2495	49.6	0.2480
2	50	0.2495	49.7	0.2485
3	25	0.1247	24.9	0.1245
4	25	0.1247	24.9	0.1245
5	10	0.0499	9.9	0.0495
6	10	0.0499	10.0	0.0500

The time required to determine the arsenic by this method was from one-half to three-quarters of an hour.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 16th, 1899.

Professor THORPE, F.R.S., President, in the Chair.

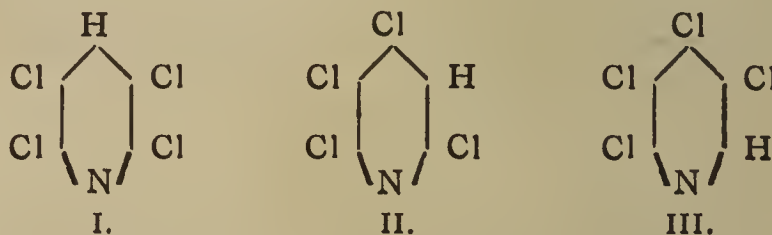
CERTIFICATES were read for the first time in favour of Messrs. Herbert William Hart, 13, Lynwood Villas, Darwen, Lancashire; Henry William Hutchin, Basset Road, Camborne.

The following Certificate was authorised by Council:—
Frank J. Pye, Towrang, New South Wales, Australia.

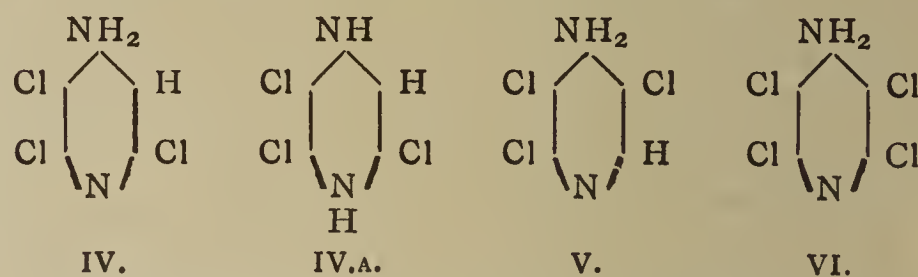
Of the following papers, those marked * were read:—

*143. "The Chlorine Derivatives of Pyridine. Part IV. The Constitution of the Tetrachloropyridines." By W. J. SELL, M.A., F.I.C., and F. W. DOOTSON, M.A.

The three theoretically possible tetrachloropyridines have all been obtained (*Trans.*, 1898, lxxiii., 432), and are represented by the formulæ I., II., and III. respectively:—



Having already proved (*Trans.*, 1897, lxxi., 1081) that the compound melting at 90—91° has the constitution represented by Formula I., the authors show in the present paper that the isomer which melts at 21—22° is represented by Formula III., and hence Formula II. must represent the constitution of the third isomer, which melts at 74—75°. Treatment with ammonia converts the compound melting at 21—22° into an aminotrichloropyridine, which is quite different from that described by Stokes and Pechmann (*Amer. Chem. Journ.*, 1886, vi., 377), and shown by them to have either the Formula IV. or possibly IV.A; as the new compound contains an amino-group in the γ -position, it must be represented by Formula V.



That the γ -position is occupied by the amino-group is evident from the fact that when this new compound is heated with phosphorus pentachloride, the aminotetrachloropyridine obtained is that which has been shown by Stokes and Pechmann, and by the authors, to have the constitution represented by Formula VI.

*144. "Contributions to our Knowledge of the Aconite Alkaloids. Part XV. On Japaconitine and the Alkaloids of Japanese Aconite." By WYNDHAM R. DUNSTAN, F.R.S., and HAROLD M. READ.

The authors have investigated the properties of the alkaloids of Japanese aconite, *A. Fischeri* ("kuza uzu"), including those of japaconitine, the crystalline toxic alkaloid examined by Wright and Luff in 1879, who assigned to it the formula $C_{66}H_{88}N_2O_{21}$. Later workers, Mandelin, Lübke, and, more recently, Freund and Beck, have asserted that japaconitine is identical with aconitine, the crystalline toxic alkaloid of *Aconitum napellus*.

The results obtained in the present investigation do not confirm these statements, but lead to the conclusion that japaconitine is a distinct alkaloid, the composition and properties of which, however, do not agree with those ascribed to it by Wright and Luff.

Japaconitine crystallises in colourless needles which melt at 204.5° (corr.). The crystallographic characters differ from those of aconitine. The base is soluble in acetone, alcohol, chloroform, and in ether, but almost insoluble in water and light petroleum. Its physiological action closely resembles that of aconitine. It contains four methoxyl groups, one acetyl group, and one benzoyl group. Its composition is provisionally represented by the formula $C_{21}H_{29}(OCH_3)_4(CH_3CO)(C_6H_5CO)NO_3$, which seems to agree best with the analytical data for the base and its derivatives. Japaconitine furnishes a series of well crystallised salts, of which the *hydrochloride* (m. p. 149—150°), the *hydrobromide* (m. p. 172—173°), the *hydriodide* (m. p. 207—208°), the *aurichloride* (m. p. 231°), and the *nitrate* (m. p. 194°) are described. Like aconitine, japaconitine is dextrorotatory, the salts being lævorotatory. The specific rotation of japaconitine is, however, much greater than that of aconitine.

When partially hydrolysed by dilute acids, japaconitine furnishes acetic acid, and a new crystalline base,

japbenzaconine, in accordance with the equation $C_{34}H_{49}NO_{11} + H_2O = C_{32}H_{47}NO_{10} + C_2H_4O_2$. It crystallises in rectangular plates which melt at $182-183^\circ$. Its lævorotation is nearly twice that of benzaconine. The salts crystallise with extreme readiness. The *hydrochloride* (m. p. 253°), the *hydrobromide* (m. p. 205°), the *aurichloride* (m. p. 228°), and the colourless *aurichloride* derivative (m. p. 178°) are described.

Japbenzaconine is hydrolysed on treatment with acids or alkalis, yielding benzoic acid and a base, *japaconine*, in accordance with the equation $C_{32}H_{47}NO_{10} + H_2O = C_{25}H_{43}NO_9 + C_7H_6O_2$. Japaconine has been obtained only in an amorphous condition, even the salts crystallise with great difficulty. The *hydrobromide* melts at 221° .

When japaconitine melts, it gradually suffers decomposition into acetic acid and a new crystalline base, *pyrojapaconitine*, $C_{32}H_{45}NO_9$. The crystalline *hydrochloride* (m. p. $175-176^\circ$), *hydrobromide* (m. p. 208° , or in another form at 241°), and *aurichloride* (m. p. 161°) are described. Both pyrojapaconitine and its salts are strongly lævorotatory.

Pyrojapaconitine is readily hydrolysed by alkalis or acids, yielding benzoic acid and *pyrojapaconine*, $C_{25}H_{41}NO_8$. Neither the base nor its salts have been crystallised.

Japaconitine yields a *triacyl*-derivative; and also a *monomethyl*-derivative by decomposition of the *methiodide* with potash.

It is evident that the properties of japaconitine and its derivatives are distinct from those of aconitine and its derivatives, although there is a strong general resemblance between the two groups.

Besides the crystalline japaconitine, Japanese aconite roots were found to contain a small proportion of its first hydrolytic product, *japbenzaconine*.

DISCUSSION.

Professor TILDEN inquired how many aconitines were known possessing the physiological action of the original alkaloid from *Aconitum napellus*, and pointed out the remarkable change in properties resulting from the elimination of the acetyl group from aconitine.

Mr. D. HOWARD said that it would be of extreme interest if any light could be thrown upon the relation of the chemical constitution of the aconite alkaloids to their physiological action, the problem being of the highest importance.

Professor DUNSTAN, in reply, stated that aconitine from *A. napellus*, pseudoaconitine from *A. ferox*, and japaconitine from Japanese aconite (probably *A. Fischeri*) exerted very similar physiological action. The relationship between the chemical constitution and the physiological action of these alkaloids and their derivatives was being investigated by Professor Cash and himself. They had already published (*Phil Trans.*, 1898, cxc., B, 239) an account of the work as far as it related to aconitine, benzaconine, and aconine, and had paid special attention to the almost entire loss of toxic power which results from the elimination of the acetyl group from aconitine. In fact benzaconine and aconine, especially the latter, were found to be, in certain respects, physiologically antagonistic to aconitine.

*145. "The Dissociation Constants of very Weak Acids." By JAMES WALKER and WILLIAM CORMACK.

A form of apparatus is described which enabled the authors to measure the electric conductivity of very weak acids with considerable accuracy, the method of experiment adopted being especially applicable to such acids as are gaseous under ordinary conditions.

The following table contains the chief results obtained, hydrochloric and acetic acids being added for purposes of comparison. The first column of figures gives the dissociation constants calculated by Ostwald's formula, the second column gives the percentage degrees of dissociation in decinormal solution, these numbers being proportional to the avidities of the acids:—

	$k \times 10^{10}$.	100 m.
Hydrochloric acid	—	91.4
Acetic acid	180,000	1.30
Carbonic acid	3,040	0.174
Hydrogen sulphide	570	0.075
Boric acid	17	0.013
Hydrocyanic acid	13	0.011
Phenol	1.3	0.0037

These results are in general harmony with the hydrolytic experiments of Shields.

DISCUSSION.

Mr. L. M. JONES asked whether the weak inorganic acids examined obeyed Ostwald's dilution law, as considerable differences occur with strong inorganic acids, and whether the dissociation in all cases proceeded with the formation of only the monovalent anion.

Mr. VERNON HARCOURT hoped that the actual measurements of the conductivity were given in the paper, and not only the inferences from these measurements. Careful physical measurements, where all conditions were recorded, had a value more certain to endure than the theory used to interpret them.

Professor TILDEN mentioned that, at his suggestion, one of his students had lately studied the conductivity and hydrolytic effects of azoimide in the expectation of finding it a tolerably strong acid. The results of these experiments, which would shortly be communicated to the Society, however, led to the conclusion that azoimide is a weak acid standing very near to hydrocyanic acid.

Professor WALKER, in reply, said that all the acids investigated obeyed Ostwald's dilution law, and that the primary dissociation in each case was therefore into one atom of hydrogen and the rest of the molecule.

Whether the theory of electrolytic dissociation were finally accepted or rejected in its present form, the "degree of dissociation" would always remain a valuable and, indeed, indispensable magnitude where aqueous solutions of electrolytes were concerned, for by its means alone is it possible to calculate chemical equilibrium in such solutions. The interpretation and the name of the magnitude might be changed, but the magnitude itself is a fundamental one.

*146. "Preparation and Properties of Solid Ammonium Cyanate." By JAMES WALKER and JOHN K. WOOD.

In a preliminary communication (*Proc.*, 1898, 108), the authors showed that pure solid ammonium cyanate might be prepared by mixing cooled ethereal solutions of ammonia and cyanic acid. The same substance can be produced by mixing ammonia gas and cyanic acid vapour at the ordinary temperature, provided the reacting gases are sufficiently diluted with some indifferent gas.

Measurements of the rate of transformation of the solid cyanate into urea showed that the rapidity of transformation increases very rapidly with rise of temperature, and that the presence of moisture greatly accelerates the action. About 3 per cent of the cyanate is decomposed, with formation of ammonia.

The molecular heat of transformation of solid cyanate into solid urea is 49K; the molecular heat of formation of solid cyanate is 738K; and the molecular heat of solution in water is -62.3K. From these numbers, it appears that the molecular heat of transformation in aqueous solution is 75K.

Ethylammonium cyanate is rapidly transformed into ethyl-urea at the ordinary temperature. When ethereal solutions of aniline and cyanic acid are mixed, the substance which separates is not phenyl-ammonium cyanate, but phenyl-urea.

*147. "Etherification of Derivatives of β -Naphthol." By WILLIAM A. DAVIS.

The author has studied quantitatively the etherification of a considerable number of substitution derivatives of β -naphthol by means of alcohol and sulphuric acid. It is shown that a single group occupying position 1 has a most

remarkable effect in limiting etherification, although the same group in position 3' exercises little influence.

The inhibiting influence of ortho-groups on the etherification of phenols, and of substituted benzoic acids, as studied by Victor Meyer and others, is fully discussed; the conclusion arrived at is that the stereochemical hypothesis proposed by V. Meyer to explain his results is not justified by facts.

The following ethers are described:—3'-bromo- β -methoxynaphthalene, m. p. 105°; 1-bromo- β -methoxynaphthalene, m. p. 82–83°; 1-chloro- β -methoxynaphthalene, m. p. 68°; 1:3'-dibromo- β -methoxynaphthalene, m. p. 100°; 3'-bromo- β -ethoxynaphthalene, m. p. 80°; 1-bromo- β -ethoxynaphthalene, m. p. 66°; 1-chloro- β -ethoxynaphthalene, m. p. 58°; 1:3'-dibromo- β -ethoxynaphthalene, m. p. 94°; 1:3'-chlorobromo- β -ethoxynaphthalene, m. p. 77°; 3'-bromo- β -propoxynaphthalene, m. p. 63.5°; 1-bromo- β -propoxynaphthalene, m. p. 35–36°; 1:3'-dibromo- β -propoxynaphthalene, m. p. 75°; and 1:3'-chlorobromo- β -propoxynaphthalene, m. p. 60.5°.

148. "On the Determination of Transition Temperatures." By H. M. DAWSON, Ph.D., B.Sc., and P. WILLIAMS, B.Sc.

While the influence of temperature on homogeneous and heterogeneous equilibrium is a continuous one, the so-called "condensed systems" are characterised by the existence of a transition temperature. At this temperature, the system suddenly undergoes a complete change. The second form of the system, which is stable at the higher temperature, is entirely re-transformed into the first on lowering the temperature below that of the transition-point.

Various methods have been employed for the determination of such transition temperatures; for example, the dilatometric, the thermometric, and the various identity methods. The latter depend upon the fact that the saturated solutions of the systems which are capable of mutual transformation become identical at the transition-temperature. In consequence of this, the properties of the saturated solutions corresponding to the various solubility curves emanating from the transition-point assume the same value at this temperature. In choosing a suitable property of the saturated solution for investigation, attention must be paid to the three following points:—(1) The property in question must be measurable accurately and rapidly; (2) it must show a notable variation for small changes in the composition of the saturated solution; (3) there should, if possible, be no loss in the quantity of the saturated solution as a result of the measurement.

The densities and electric conductivities of saturated solutions have been investigated by the authors with a view to determining transition temperatures. The density measurements were carried out with the saturated solution of sodium sulphate. The curves obtained by plotting the density intersect at a wide angle at 32.4° corresponding to the transformation of the decahydrate into the anhydrous salt at this temperature.

Conductivity measurements were also carried out with this salt; as in the case of the density, two curves intersecting at about 32.5° were obtained.

The change in direction of the curve at this temperature is not so great as was expected; this, is, however, explicable on the ground that the solutions are so concentrated.

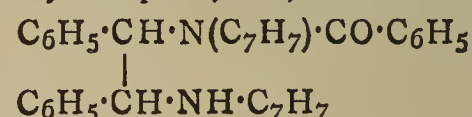
A second series of experiments was carried out with thorium sulphate, the nonahydrate of which, according to Roozeboom, changes into the tetrahydrate at about 43°. The concentration of the saturated solution at the transition-temperature is, in this case, only about one-third normal.

On plotting the conductivity on a diagram, two curves are obtained intersecting at about 48°. To confirm this result, the transition temperature has been determined dilatometrically and tensimetrically, by which methods

46.5° and 47.5° were obtained. Roozeboom's determination of 43° would therefore appear to be somewhat too low. The authors point out the availability of the above methods of determination in cases where other methods cannot be used with advantage.

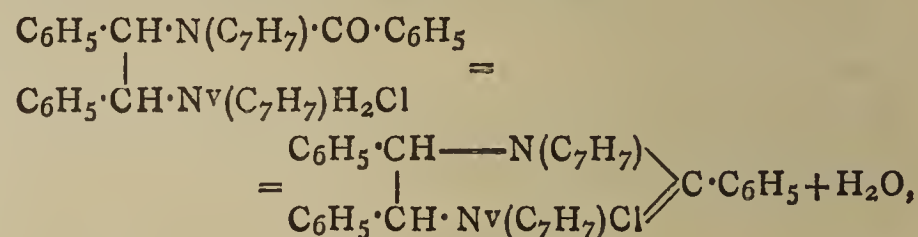
149. "Constitution of Amarine, of its supposed Dialkyl- and Diacyl-derivatives, and of Isoamarine." By FRANCIS R. JAPP, F.R.S., and JAMES MOIR, M.A., B.Sc.

The author's find that Claus and Elbs's "dibenzylamarine" (m. p. 139–140°) has in reality the composition represented by the formula $C_{21}H_{18}(C_7H_7)_2N_2O$, and is benzoyl-s-dibenzyl-i-diphenylethylenediamine,—



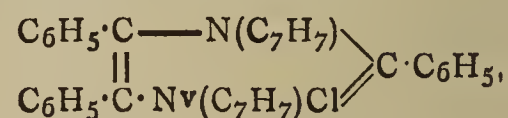
It may be obtained, along with a dibenzoyl-derivative (m. p. 268°), by the action of benzoic chloride on Grossmann's s-dibenzyl-i-diphenylethylenediamine, thus proving its constitution. This dibenzoyl-derivative, melting at 268°, may also be obtained by introducing a benzoyl-group into "dibenzylamarine." Claus and Elbs's "dimethylamarine" (m. p. 146°) is in reality the corresponding benzoyl-s-dimethyl-i-diphenylethylenediamine, and Borodine's "diethylamarine" (m. p. 110–115°; the authors find 125°) is the corresponding diethyl-derivative.

When benzoyl-s-dibenzyl-i-diphenylethylenediamine hydrochloride is heated to 220°, it parts with water, yielding dibenzylamaronium chloride,—

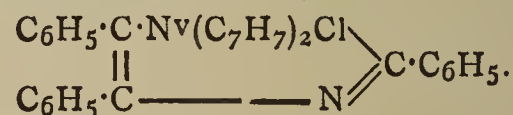


a reaction which proves conclusively the constitution of the dialkylamaronium salts.

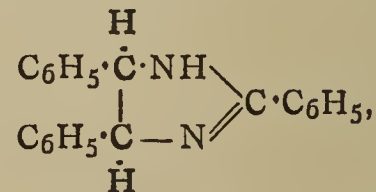
Dibenzylamaronium chloride gives a dichromate of the formula $(C_{35}H_{31}N_2Cl)_2 \cdot H_2Cr_2O_7$ (m. p. 173°), which, when boiled with glacial acetic acid and a little hydrochloric acid, yields dibenzyllophonium chloride, showing that the latter substance has the constitution—



instead of, as suggested by Japp and Davidson,—



The authors regard amarine as 2-phenyl-4:5-cis-diphenyl-4:5-dihydroimidazole,—



employing the numbering of the imidazole ring adopted by M. M. Richter. A formula identical with the foregoing, excepting that the configuration was not indicated, was put forward by Claus.

Amarine is thus a meso-form derived from Grossmann's i-diphenylethylenediamine (m. p. 120–121°), which this author obtained by the reduction of amarine.

The authors show that Snape and Brooke's isoamarine is 2-phenyl-4:5-trans-diphenyl-4:5-dihydroimidazole—the corresponding racemic form. With Professor Snape's permission, they reduced isoamarine with sodium in boiling alcohol, and obtained, as in Grossmann's analogous experiment with amarine, a benzylidene derivative, which on hydrolysis with acids, gave benzaldehyde and a base—in this case Feist's γ -diphenyl-

ethylenediamine (m. p. 90—92°). Isoamarine is thus related to Feist's base, in the same way as amarine to Grossmann's. Feist's base (prepared by the reduction of α -benzildioxime), when heated with benzoic acid at 170—180°, yielded isoamarine, thus confirming the foregoing view as to the constitution of the latter compound. Amarine benzoate undergoes no change at this temperature.

Isoamarine may be readily prepared by fusing amarine with sodium, or by heating amarine hydrochloride above its melting-point.

The authors find that Claus and Scherbel's supposed dibenzoylamarine is identical with Grossmann's *s*-dibenzoyl-*i*-diphenylethylenediamine, and that Bahrmann's supposed diacetylamarine is acetylbenzoyl-*i*-diphenylethylenediamine. This removes the supposed evidence for the symmetrical or di-imidic formula of amarine.

The authors have made a detailed study of the reactions of the supposed dibenzylamarine, the results of which confirm the foregoing views as to its constitution.

150. "The Atomic Weight of Nitrogen." By G. DEAN, B.A.

The work of which an account is given in this paper is in continuation of that of which a preliminary notice has already been communicated to the Society (*Proc.*, 1898, xiv., 174). After giving a summary of the results of previous workers, the author deduces a mean value from them of 14.034 for the atomic weight of nitrogen, but points out that the means of the determinations by chemical methods of individual workers vary from 13.975 (Pelouze) to 14.05 (Stas). The ratio of the densities of oxygen and nitrogen as determined by Lord Rayleigh and by M. Leduc is 16:14.003. These variations seemed to be too great, so it was thought that it would be both important and interesting to try a new method which would involve as few atomic weights as possible, and only those which are known with the highest accuracy. Silver cyanide was selected as the compound containing nitrogen, and the ratio between a given mass of it and that of the potassium bromide required for the complete precipitation of the silver contained in it determined with all the precautions insisted on in such work by Stas. The cyanide was decomposed in some cases by dissolving it in nitric acid, in other experiments sulphuric acid. The ratio between the purest silver and the sample of potassium bromide used was carefully determined, so that the ratio found was really Ag:AgCN. This was found to be 107.93:133.962, whence CN=26.032 and N=14.031 if C=12.001.

ROYAL INSTITUTION.

General Monthly Meeting, December 4th, 1899.

Sir JAMES CRICHTON-BROWNE, M.D., F.R.S., Treasurer and Vice-President, in the Chair.

THE following were elected Members:—Professor H. E. Armstrong, F.R.S., and Messrs. J. H. Bowman, J. S. Brookfield, J. B. Carrington, W. B. Cloete, and L. Leigh Smith.

The following letter from the Clerk of the Goldsmiths' Company was read:—

"Goldsmiths' Hall, London, E.C.,
November 16th, 1899.

"DEAR SIR,—

"I am directed to inform you that the attention of the Court of the Goldsmiths' Company having been drawn to the fact that the Royal Institution of Great Britain has lately celebrated its Centenary, they have, in order to mark their sense of the importance of that event, been pleased to make to the Institution the further grant of £1000, for the continuation and development of original research, and especially for the prosecution of further investigations

of the properties of matter at temperatures approaching that of the absolute zero of temperature.

"I enclose a cheque for this amount, and I shall feel obliged to you to acknowledge the receipt.—I am, dear Sir, Your obedient Servant,

(Signed) WALTER S. PRIDEAUX.

"The Hon. Secretary,
The Royal Institution of Great Britain."

The following resolution (proposed by the Lord CHANCELLOR and seconded by Sir A. NOBLE) was then passed:—

"That the Members of the Royal Institution of Great Britain, in General Meeting assembled, having been informed that the Court of the Goldsmiths' Company have made a donation of £1000 to the funds of the Royal Institution in commemoration of its Centenary, and in aid of the investigations which are being carried on in its Laboratories into the properties of matter at low temperatures, desire to express to the Court their profound and grateful appreciation of this second munificent manifestation of their practical interest in the work of the Institution—a manifestation which has been made on this occasion at once reminiscent of past services to science and prescient of services yet to come."

NOTICES OF BOOKS.

Science Sketches. Chemistry, its Evolution and Achievements. By FERDINAND G. WIECHMANN. New York: William R. Jenkins. 1899. Pp. viii.—176. 16 mo.

DR. WIECHMANN, who is already known to chemists by his works on Sugar Analysis and Theoretical Chemistry, now offers a modest volume that attempts to enlist the interest of non-professional readers in an exact science. He sketches the history of chemistry from its obscure birth through the ages down to the present time, following somewhat the same lines as those of Hermann Kopp, and narrates—briefly of course—the most notable achievements of the science in its technical applications. The work is not divided into chapters, but marginal notes in full-faced type serve the same purpose.

It is ungenerous to point out omissions in a work of 176 pages, the subject of which covers such an enormous field; it is more just to give credit for inclusions than to criticise exclusions. The Index of Names has a good feature; each name in the alphabetical list bears the birth-date and death-date of the person. In the list of works consulted we miss the grand volumes by Berthelot ("Collection des Alchimistes Grecs," and "La Chimie au Moyen Age").

Whether the author has really succeeded in portraying the "grandeur and the charm of the science" in such a fashion as to attract non-professional readers, can but be determined after the book has been some time before the public; his attempt is praiseworthy, yet many paragraphs can only be appreciated by the educated chemist already familiar with the growth of the science.

The primary caption of the title-page, "Science Sketches," intimates that this book is the first of a series, but the preface makes no allusion to this.

Index to the Literature of Zirconium. By C. LANGMUIR and CHARLES BASKERVILLE. Smithsonian Miscellaneous Collections, 1173. Washington City: Published by the Smithsonian Institution. 1899. 29 pp. 8vo.

THIS "Index" was begun independently by the two authors, who live one thousand miles apart; an announcement in the "Fourteenth Annual Report of the Committee on Indexing Chemical Literature" (appointed by the American Association for the Advancement of Science

in 1882) directed the attention of one of the chemists to the undertaking begun by the other, and after correspondence they wisely joined forces and produced the present booklet. It bears the endorsement of the Committee just named, and forms one of the series that now embraces the following elementary substances:—U, Mn, Ti, Vd, Cb, Di, Ce, La, Pt, Pd, Ir, Rh, Os, Ru, and Tl, besides many other topics. The first-named and the last ten have appeared in the publications of the Smithsonian Institution.

The bibliography of zirconium begins with the discovery by Klaproth in 1789, and is brought down to the end of the year 1898; the total number of references being 248, exclusive of reproductions and abstracts.

All publications by the Smithsonian Institution, of Washington, D.C., are for sale at low prices, merely to cover printing and paper. The agents of the Institution for Great Britain are Messrs. Wesley and Son, 28, Essex Street, Strand, London. H. C. B.

The Chemistry of Soils and Fertilisers. By HARRY SNYDER, B.Sc. Easton, Pa. 1899, Pp. 277.

THE proper use of manures is a problem which is by no means yet thoroughly worked out and understood: as our knowledge of chemistry advances we know more and more what a manure should be, and that organic nitrogen is the predominant constituent required. It has already been pointed out by Sir William Crookes that the yield of wheat depends, to a very great extent, on the amount of nitrogen in the soil: this subject must not be lost sight of, and we are glad to see that Mr. Snyder fully recognises the importance of the question.

He treats the whole matter in a thorough manner from the time of De Saussure, Davy, and Boussingault, to the present time. The long-continued experiments of Gilbert and Lawes receive due attention, as also do those of Ville: we are, however, sorry to see that in spite of political approachments England and the United States are slowly but surely drifting apart. This book is written, not in the English, but in the American language.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 20, November 13, 1899.

Preparation and Properties of Crystalline Phosphides of Strontium and Barium.—A. Jaboin.—By means of the electric furnace, the author has prepared crystalline phosphides of strontium and barium. The corresponding phosphates are reduced by means of carbon. Analysis shows these two bodies to have the composition P_2Sr_3 and P_2Ba_3 . They are very stable, but possess great chemical activity. They decompose water at ordinary temperatures, giving phosphoretted hydrogen and the hydrate of barium or strontium.

Estimation of Phosphorus in Organic Compounds.—Ch. Marie.—In the course of researches on organic compounds containing phosphorus, the author finds that the employment of potassium permanganate in nitric solution to oxidise the phosphorus is not satisfactory. He therefore modifies the method by dissolving the substance to be analysed in excess of strong nitric acid and adding the permanganate little by little. This method has been compared with the ordinary method of oxidation in sealed tubes, and is found to give much better results, even in

the case of compounds very difficult to oxidise, such as ammoniaco-calcic aceto-diphosphite.

New Asymmetric Compounds of Nitrogen obtained by Synthesis and possessed of Rotatory Power.—W. J. Pope and S. J. Peachey.—(See p. 252).

MEETINGS FOR THE WEEK.

MONDAY, 11th.—Society of Arts, 8. (Cantor Lectures). "Enamelling upon Metals," by Henry Hardinge Cunyngname.
WEDNESDAY, 13th.—Society of Arts, 8. "Sea Angling and Legislation," by F. G. Affalo.
THURSDAY, 14th.—Society of Arts, 4.30. "Round about the Andamans and Nicobars," by Colonel R. C. Temple, C.I.E.

THE DAVY FARADAY RESEARCH LABORATORY OF THE ROYAL INSTITUTION.

Directors:

The Right Hon. LORD RAYLEIGH, M.A., D.C.L., LL.D., F.R.S.
Professor DEWAR, M.A., LL.D., F.R.S.

Superintendent of the Laboratory:

Dr. ALEXANDER SCOTT, M.A., D.Sc., F.R.S.

This Laboratory was founded by Dr. LUDWIG MOND, F.R.S., as a Memorial of Davy and Faraday for the purpose of promoting, by original research, the development and extension of Chemical and Physical Science.

The Laboratory is open free of charge to Workers of either sex, and any nationality, prosecuting individual investigations; and the extensive collection of Physico-Chemical Apparatus presented by the Founder is available for their use, together with such materials, chemicals, electricity, &c., as the Directors may authorise.

Assistants and a trained mechanic are attached to the Laboratory to aid Workers in the prosecution of their researches.

All persons desiring to be admitted as Workers must send evidence of scientific training, qualification, and previous experience in original research, along with a statement of the nature of the investigation they propose to undertake.

MICHAELMAS TERM.—Monday, October 2, to Saturday, December 16.

LENT TERM.—Monday, January 8, to Saturday, April 7.

EASTER TERM.—Monday, April 30, to Saturday, July 28.

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THE CHEMICAL NEWS.

VOL. LXXX., No. 2090.

GOLD-ALUMINIUM ALLOYS.*

By C. T. HEYCOCK, F.R.S., and F. H. NEVILLE, F.R.S.

THE first part of this paper gives the equilibrium curve for the liquid alloys and the various solid bodies that can form in them. The curve is based on the determination of the freezing points of mixtures varying in composition from pure gold to pure aluminium.

The freezing points were determined by means of platinum resistance pyrometers of the Callendar-Griffiths type, and the composition of each alloy was found by extracting a sample from the crucible and analysing it.

The ordinate in the curve is the freezing point on the air-centigrade scale, and the abscissa is the composition of the alloy expressed in atomic percentages of aluminium.

The curve was found to consist of seven branches, each branch corresponding to a state in which a particular solid crystallises first. In harmony with this, seven substances can be detected in the solid alloys. The bodies are:—

Gold; Au_4Al ; Au_5Al_2 or perhaps Au_8Al_3 ; Au_2Al ; a body which is probably $AuAl$; $AuAl_2$, Roberts-Austen's purple alloy; aluminium.

The bodies Au_2Al and $AuAl_2$ † are indicated by well-marked summits in the curve, at 33.4 and at 66.6 atomic per cents. of aluminium respectively.

The melting or freezing point of Au_2Al is at 625° C., that of $AuAl_2$ is at 1062° C., apparently identical with the melting point of gold itself. The body whose formula we give as either Au_5Al_2 or Au_8Al_3 has its melting point at 575° C. The body Au_4Al has its melting point near 550° C. That of the hypothetical $AuAl$ is not given by the curve.

The curve has three well-marked eutectic angles. One of these is at 527° C. and 3.6 per cent by weight of aluminium, the alloy here being a mixture of Au_4Al and Au_5Al_2 . The next is at 569° C. and 8.36 per cent by weight of aluminium; this alloy has a composition corresponding to the formula Au_3Al_2 , but it is a mixture of Au_2Al and $AuAl$. The third eutectic is at 648° C., and the alloy contains 1.87 per cent by weight of gold; it is a mixture of $AuAl_2$ and aluminium. We see from the above that the mixture with the lowest melting point of all is that containing 3.6 per cent by weight of aluminium, this small percentage depressing the melting point of gold from 1062° C. to 527°, that is more than 500°. A liquid of this composition, though almost wholly composed of gold, will not begin to solidify until this comparatively low temperature of 527° C. is reached.†

Each of these eutectic points gives rise to a horizontal row of second freezing points in the curve, and the alloys containing more than 44 and less than 60 atomic per cents of aluminium have three distinct freezing points corresponding to the successive formation of three solid bodies.

The four compounds, Au_4Al , Au_5Al_2 , Au_2Al , and the hypothetical $AuAl$, are pure white substances. $AuAl_2$, as is well known from the work of Sir W. Roberts-Austen, is a magnificent purple body.

The latter part of the paper gives the result of a

microscopic examination of polished and etched sections of alloys taken from various parts of the curve. All the bodies referred to above could be distinguished under the microscope. The photomicrographs accompanying the paper show that the structure of the solid alloy is everywhere in strict harmony with the indications of the freezing point curve. Speaking generally, we may say that the patterns observed in the photographs repeat themselves at corresponding points of each branch of the curve. For example, near the summit of the branch corresponding to the pure alloy, Au_2Al , the photograph shows us more or less hexagonal polygons of this substance almost entirely filling the field, and only separated from each other by very fine lines of impurity. If we take a section of an alloy a little way below the summit, we see the polygons of Au_2Al surrounded by a ribbon-like network of mother substance. Still further down, the crystals of Au_2Al are scanty, and arranged in such regular patterns, generally in lines at right angles to each other, as to render it certain that they crystallised freely while surrounded by liquid. Finally, at the bottom of the branch, that is at the eutectic point, the large crystals of Au_2Al are absent, and the whole field is full of the mother substance, which is sometimes but, as we explain in the paper, not always a eutectic mixture.

If, leaving the eutectic point, we ascend the next branch, these phenomena repeat themselves, but the primary crystallisation (that is the matter which solidified first) is now of a different substance.

Some of the photographs of alloys very rich in aluminium were taken by the Röntgen rays, and an enlargement made from the negative. The contrast between the Röntgen ray photograph and the surface photograph of the same alloy shows what a much better picture of the structure of the alloy is given by the Röntgen rays.

ATOMIC WEIGHT OF THE METAL IN RADIFEROUS BARIUM CHLORIDE.

By Madame SKŁODOWSKA CURIE.

M. CURIE, M. Bémont, and I have already published a research, in the course of which we showed that the barium compounds extracted from uranium mineral possessed great radio-activity. We also stated that we believe this activity to be due to a new element—radium.

The barium salts extracted from uranium minerals are only distinguished from barium salts from other sources by their radio-activity. The lines of barium are seen with the spectroscope, and the atomic weight agrees with that of barium.

By fractionation it is possible to concentrate the radio-activity so as to obtain more and more active products.

M. Demarçay has studied the successive fractions spectroscopically. He was able to discover a new spectrum in the latter fractions, some of the lines attaining the same intensity as the barium lines.

I have determined the atomic weight of the metal in successive fractions, and I find that the atomic weight of strongly radio-active barium is greater than that of ordinary barium, and that the difference increases with the activity.

I fractionally crystallised 2 kilos. of purified radiferous barium chloride, which was extracted from half a ton of residue from uranium mineral. This treatment concentrated the radio-activity in the least soluble parts. I then obtained several fractional precipitations with alcohol from the most active portion; the activity concentrates in the precipitated portions.

The radiferous barium chloride so obtained is treated with sulphuretted hydrogen to eliminate the small quantity of lead present; after this it contains no further perceptible impurity.

I determined the atomic weight of the metal by esti-

* Abstract of a Paper read before the Royal Society, Dec. 7, 1899.

† The rapid depression in the freezing point of gold, due to the presence of small quantities of aluminium, and the great rise in the freezing point as the composition corresponding to the compound $AuAl_2$ is approached, have been already discovered by Sir William Roberts-Austen.

mating the chlorine in the anhydrous chloride by silver nitrate. The weight of chloride used was about 0.5 gm.

Each determination of the atomic weight of the metal in the active chloride was accompanied by a control experiment on inactive barium chloride.

The activity of the barium chloride before fractionation was about sixty times greater than that of uranium, but to obtain a difference in atomic weight, it was necessary to have an activity several thousand times greater than that of uranium.

In the following table, i denotes the electric current which the active barium chloride produces when it occupies a circular surface of 2 c.m. diameter at the centre of one of the plates of a condenser of the following dimensions:—Diameter of plates, 8 c.m.; distance between plates, 3 c.m.; difference of potential between the plates, 100 volts. The current which metallic uranium gives under these conditions is equal to 0.25×10^{-11} ampères. a Denotes the radio-activity of the active chloride, that of uranium being taken as 1. m Denotes the atomic weight of the metal in the radio-active chloride; and Ba , the atomic weight found for barium in the control experiment.

i (10^{-11} ampères).*	a .	m .	Ba .
750	3000	140.0	138.1
1170	4700	140.9	137.6
1870	7500	145.8	137.8

* In the original this reads 10^{+11} ampères, which must be a mistake for 10^{-11} .

There is seen to be a very decided difference between the atomic weight of barium and that of the last fraction.

The radiant properties of each specimen were measured directly after preparation in a dry state. Indeed, the radio-activity of all the radiferous chlorides of barium increases considerably for several days after passing from solution into the solid state, whether by crystallisation (chloride) or by precipitation (sulphate, carbonate). This activity seems to reach a limiting value by the end of some weeks, which, for very active compounds, may be five or six times as great as the initial value.

The specimen of which the spectrum was described by M. Demarçay started with $a = 17,000$. I had not enough of this left for an atomic weight determination.

Both my experiments and the spectrum examination seem to prove that the hypothetical element which we have called radium does, indeed, exist, and that it possesses an atomic weight slightly higher than that of barium.—*Comptes Rendus*, cxix., No. 20.

RELATIONS BETWEEN THE ATOMIC WEIGHTS AND PHYSICAL PROPERTIES OF ELEMENTS.

By THOMAS BAYLEY.

THE following facts, which show a connection between the atomic weight and certain physical properties of the elements, have not been recorded, as far as I am aware.

The product of melting-point (absolute) \times coefficient of linear expansion is approximately a constant for certain elements. For Cd it is 0.0197, for Zn 0.0205, for Cu 0.022, for In 0.020, for Pd 0.021, for Ir 0.0193, for Pt 0.018, for Bi 0.0216, for Au 0.0196. The product is somewhat higher for these:—Mg 0.024, Ag 0.024, S 0.025, Na 0.026, K 0.028.

Taking the products as equal, then two cubes of (say) Zn and Cd, of equal dimensions at absolute zero, will have equal volumes at the respective melting-points. The weights of the cubes are as sp. gr. Cd : sp. gr. Zn, and the number of atoms in each as—

$$\frac{\text{Specific gravity Cd}}{\text{Atomic weight Cd}} : \frac{\text{Specific gravity Zn}}{\text{Atomic weight Zn}}$$

Dividing the expansion among the atoms to obtain the atomic expansion (absolute zero to melting-point), we get—

$$\frac{\text{Expansion}}{\text{Specific gravity}} = \frac{(\text{Atomic weight}) \text{ Expansion}}{\text{Specific gravity}} =$$

Atomic volume \times Expansion. The expansion is directly as the atomic volume.

Again,—

$$\text{Specific heat} \times \text{melting-point (abs.)} \times \text{atomic weight} = \text{atomic heat (absolute zero to melting-point)}.$$

Let—

$$\frac{\text{Specific heat} \times \text{melting-point}}{\text{Atomic weight}} = x,$$

then—

$$\text{Specific heat} \times \text{melting-point} = x \text{ atomic weight},$$

and by substitution—

$$\text{Atomic heat (absolute zero to melting-point)} = x (\text{atomic weight})^2.$$

The values of x are for—

K = 1.415	Au = 0.2172	N = 0.997	Ga = 0.3426
Na = 4.372	Ag = 0.6425	P = 2.066	Zn = 1.01
	Cu = 2.02	Sb = 0.394	Cu = 2.02
		Bi = 0.0796	

In = 0.2246	Hg = 0.03725	Pt = 0.335
Ag = 0.6425	Au = 0.2172	Pd = 1.01

It will be observed that, in Group I., the value of x for K is closely approximate to one-third of the value for Na, the value for Au is one-third that for Ag, the value for Ag is one-third that for Cu. The values of x for Group V. are for $N = \frac{1}{2} P$, for $Sb = \frac{1}{2} P$, $Bi = \frac{1}{2} Sb$. Similarly, x for $Zn = \frac{1}{2} Cu$, for $Ga = \frac{1}{2} Cu$, $In = \frac{1}{2} Ag$, $Hg = \frac{1}{2} Au$, $Pt = \frac{1}{2} Pd$. Of course, specific heat varies with temperature, but a similar consideration applies to Dulong and Petit's law of atomic heats.

December 6, 1899.

AMMONIUM MOLYBDATE AS A DELICATE REAGENT FOR STANNOUS CHLORIDE.

By J. P. LONGSTAFF.

FRESENIUS, in his "Qualitative Analysis" (English translation, 10th edition, p. 184), says that the hydrochloric acid solution of molybdic acid is coloured "immediately on addition of stannous chloride, the colour being brown, green, or blue, according to the proportion of reducing agent and the concentration of the solution." This reaction is the basis of a well-known test for molybdic acid, and is given among the reactions of molybdates in text-books of qualitative analysis. So far, however, as I have been able to ascertain after careful search, it does not appear that molybdic acid has ever been proposed as a reagent in testing for stannous chloride; and this seems very remarkable, as I find that ammonium molybdate (the ordinary laboratory reagent) is not only a suitable reagent, but that, for very dilute solutions of stannous chloride, it affords a much more delicate test than mercuric chloride does. I think, therefore, that it may be useful if I give the main results I have arrived at.

The solutions tested were prepared by dissolving small quantities—varying from 7 m.grms. to 4 c.grms.—of pure tin (as supplied by Harrington) in hot concentrated hydrochloric acid, and at once diluting to a litre or other suitable definite volume. Measured quantities were drawn off by a pipette and at once diluted, and, in this way, solutions of various concentrations, but all containing very small quantities of tin, were obtained. It was found necessary to carry through each experiment as rapidly as possible,

since very dilute stannous solutions undergo oxidation in a remarkably short time. For instance, in my first experiment, ordinary distilled water was used, and the solution, which contained 0.0230 grm. of tin in a litre, gave no indication of the presence of stannous chloride at the end of half an hour. The oxidation had evidently been effected by means of air dissolved in the water. In subsequent experiments recently boiled-out water was always employed.

By using all reasonable precautions to prevent oxidation, I find that, for ordinary test-tube work, the addition of ammonium molybdate to, say, 10 c.c. of a stannous chloride solution, of a dilution corresponding to 1 part of tin in anything up to 100,000 parts of solution, gives a very distinct blue colouration.

The delicacy of the test is, however, much greater than this. For instance, 0.0103 grm. of tin dissolved in hydrochloric acid was diluted to 100 c.c.; 1 c.c. of this solution, when diluted with 150 c.c. of water, still gave a perceptible colouration with ammonium molybdate. This corresponds to a dilution of 1 part of tin in 1,500,000 of solution. The presence of the blue colour was rendered distinct by placing the beaker containing the solution and reagent beside another containing only water and reagent, the two liquids being of equal volume; when a sheet of white paper was held behind the beakers, the difference in colour of the liquids was rendered perfectly distinct.

Solutions of greater dilutions than the last mentioned were not prepared.

If, in laboratory practice, the tin is separated from the other metals of the arsenic group by reduction with zinc and hydrochloric acid, the zinc with the tin deposit upon it should be carefully washed with water, completely dissolved in concentrated hydrochloric acid, and the solution so obtained diluted with water. Ammonium molybdate should then be added, and, if tin is present, even in very minute quantity, a distinct blue colour will appear. This colour, which slowly disappears on exposure to the air, is at once discharged by the addition of concentrated hydrochloric acid. Hence a strongly acid solution must always be diluted before applying the test.

Pure zinc deposits tin very slowly, so that, in order to get down enough to give a distinct reaction with mercuric chloride, when it is dissolved in hydrochloric acid, the process of reduction must be allowed to go on for a considerable time; but this is not necessary when ammonium molybdate is to be used as the test reagent, since a trace of tin, which will give no visible precipitate with the former, gives at once a perfectly distinct colouration with the latter.

Of course, whether the zinc to be used be "pure" or not, a quantity of it should be completely dissolved in hydrochloric acid, and, after dilution, the liquid should be examined for tin in the way I have indicated. If this is found to be present, of course such zinc is absolutely useless for the purpose of analysis.

So far as my experience goes, laboratory students have great difficulty in conclusively proving the presence or absence of tin, in a complex mixture, by the ordinary methods of qualitative analysis. In the method ordinarily employed, the sulphides of antimony and tin (always SnS_2 after treatment with yellow ammonium sulphide and reprecipitation) are boiled up with strong hydrochloric acid, the solution is evaporated to get rid of most of the acid, and is then diluted with water. Platinum foil and zinc, in contact, are then used to precipitate antimony and tin. As previously pointed out, however, the tin comes down very slowly, and, when it is (with the zinc) dissolved in hydrochloric acid, and the solution concentrated to a very small bulk, it is frequently found that mercuric chloride gives no precipitate whatever, and sulphuretted hydrogen only a trace of precipitate or a faint colour, either of which may be caused by a small quantity of antimony. Now, neither arsenious chloride nor antimonious chloride gives a blue colour with ammonium molybdate; and

therefore I venture to say that this reagent will, on taking the precautions already pointed out, indicate with ease and certainty the presence or absence of tin.

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REMINISCENCES OF BUNSEN AND THE HEIDELBERG LABORATORY,

1863—1865.*

By HENRY CARRINGTON BOLTON, Ph.D.

I FIRST met Bunsen in the lovely, retired valley of Engelberg, Switzerland, during the summer of 1863; I had spent the preceding twelve months in Paris, working in Dumas's laboratory at the Sorbonne, and in the Ecole de Médecine under Wurtz, and was expecting to continue my studies in Heidelberg. Learning by accident that Bunsen was at an adjoining *Gasthaus*, I called on him and told him of my plans; he received me graciously, and immediately won my heart by his affability, by the charming smile that lit up his large features, and by his unselfish interest in my personal affairs. Being myself quite ignorant of the German language we conversed in French, and he gave me useful hints as to the opening of the University laboratory.

My first semester at Heidelberg was devoted almost exclusively to laboratory work, but I attended Bunsen's lectures on general chemistry every morning at nine o'clock in the adjoining auditorium. Bunsen's habit of saying one word when he meant to use another was at first puzzling, particularly as I was very weak in German, but when he exhibited the violet vapour of iodine and called it chlorine my previous knowledge of chemistry assisted comprehension. After every lecture Bunsen rarely missed spending several hours in the laboratory, going from student to student with enquiries, suggestions, and useful hints. Desirous of securing my share of this personal contact, I soon found the best way to induce the Hofrath to linger was to have a supply of clean test-tubes and beakers on an orderly desk, with a query or two requiring experimental answers. Any suggestion as to the use of the spectroscope in connection with a substance under examination was sure to interest the Professor, as that famous instrument was a comparatively new adjunct to chemical work, being then about four years old.

When in the laboratory Bunsen habitually carried between his lips a short, unlighted cigar, and he often stopped at a student's desk only long enough to light the tobacco at a "Bunsen" burner; in a few minutes the cigar was again without a spark owing to his absent-minded neglect to pull on it. Absent-mindedness was a marked trait in Bunsen's character, and many amusing anecdotes are told of the difficulties it brought him. The statement that he remained a bachelor because he forgot his wedding-day is, of course, apocryphal, as is the other about his putting on a suit of garments on top of others that he had forgotten to take off; but the following came under my personal observation. Bunsen used to dine every day at a little table reserved for him in a restaurant connected with the hotel in which I lived; one spring he fell into the habit of ordering veal-cutlets and asparagus as the chief item for his meal, and, without reflection or feeling that a change of diet would be agreeable, he continued to order "*Kalbs-cotelette und Spargel*," daily for several weeks, until one day the *Kellner* gravely informed him that asparagus was no longer in season and could not be supplied. Bunsen seemed to be immensely taken aback, and to realise for the first time that he had been dining on one dish for a long period; he soon recovered himself, however, and asked the waiter for the bill-of-fare, from which, after careful examination, he ordered mutton-

* Advance proofs from *Science*.

chops and pease, and this was his daily diet up to the time I changed my hotel.

When the laboratory was closed for the Christmas holidays I tried to get permission to work in the deserted rooms, but in vain, and not wishing to be idle I worked at growing crystals, improvising a desk out of a hotel wash-stand, and a heater out of the huge porcelain stove. Some time after I showed to Bunsen a single crystal of copper-calcium acetate about 3 inches long, with perfectly regular facets, and of which I was quite proud; he looked at it rather solemnly, as I thought, and enunciated the single word "*ausgezeichnet*." This was not in my limited vocabulary, and whether a commendation or a disapproval I could not divine; I puzzled over the word all day, and on returning home the dictionary explained its meaning to my great satisfaction.

As my knowledge of German increased I attended the lectures of Kirchhoff and of Kopp, but I never was able to enjoy the latter's interminable sentences and involved style.

Bunsen's assistants in the laboratory at the time of my sojourn were Dr. Bender and Dr. Rose; the latter had the reputation among the students of giving more accurate instruction in mineral analysis than Bunsen himself. Rose is now professor in the University of Strassburg.

Bunsen's methods in mineral analysis were not wholly approved of by the students; one day he stopped at my desk for a moment, and picking up a filter containing a moist precipitate he inquired: "What have you here?" Seeing with consternation a portion of my *quantitative* precipitate sticking to his thumb, I hastily seized a "*Spritz-flasche*," and washed the substance off his thumb into the filter on the funnel before venturing a reply. Bunsen smiled genially and passed on to my neighbour.

Bunsen showed extraordinary callousness to heat, being able to hold in his fingers metal nearly red hot; on one occasion when stirring a glowing crucible with a very short spatula, his skin fairly sizzled and for relief he took hold of the lobe of his ear with his smoking thumb and fore-finger, explaining that the ear was the coolest part of the body.

The celebrated Dr. C. R. Fresenius, of Wiesbaden, having appropriated some discovery or method of Bunsen, without giving credit, was cordially disliked by him, and he once showed it by a significant act. A student accosted the Hofrath as he passed by and put to him some simple question in analytical chemistry; on the desk lay open a copy of Fresenius's "*Anleitung*," whereupon Bunsen closed the book with a deprecatory gesture, pulled out the drawer of the student's desk to its extreme limit, and thrust into it as far back as possible the objectionable volume, saying: "*Nun, mein Herr, we will proceed.*"

Bunsen was rather sensitive to criticism; one of my American colleagues tells me of an incident illustrating this. The professor proposed to the student the joint preparation of certain caesium and rubidium salts, saying he would secure several barrels of the mineral water rich in the chlorides, and would have the water boiled down to a small volume ready for the separation of the rare elements. The American felt highly pleased at the flattering proposal, and to show his interest in the matter mentioned that he had studied under Professor O. D. Allen, of New Haven, who had done work on caesium and rubidium. This was an unfortunate remark, however, for Allen had corrected Bunsen's figures for the atomic weight of Cs, and the Hofrath remembering this never again mentioned the subject to my friend.

In those days students were obliged to prepare some substances now commonly provided, and to construct some apparatus with their own hands. Every student had to etch and calibrate his own eudiometer, and some of them wasted much time over the hydrofluoric acid process before getting good results. I remember, too, purifying potassium hydroxide by solution in alcohol (an extra charge), and evaporation in a large silver basin loaned by an assistant. One green, Russian student bought at

Desaga's, potassium cyanide instead of the hydroxide, and was vainly trying to dissolve it, walking about the laboratory shaking the bottle for hours, when Bunsen noted its singular appearance, caused the operation to be suspended, and on ascertaining the nature of the substance cautioned the student against it.

Speaking of Russians reminds me of an amusing occurrence: one of them was instructed to precipitate a substance "*mit überschüssigem Kali*" and not finding any bottle labelled "*überschüssiges Kali*," he inquired for it of a neighbour, who mischievously sent him to Dr. Bender, telling him the article was kept under lock and key with other costly substances, such as silver nitrate and platinum chloride. The astonished assistant explained to the Russian that an *excess* of potash did not require a special bottle; the student was nicknamed "*Überschüssiges Kali*" for the rest of the semester.

Many nationalities were represented in Heidelberg laboratory; besides Russians there were Bessarabians. Hollanders, Bohemians, Germans from North and from South, Austrians, one Chilian, one Englishman (the late Dr. Walter Flight, F.R.S.), one Scotchman (Mr. Sims), one Irishman (Mr. John Price), and several Americans, fifty-nine students in all, of which fifty-eight were incessantly smoking; the fumes of tobacco mingled with vapours of H_2S , SO_2 , HNO_3 , and NH_3 , making an atmosphere so thick that I regret not having cut off a slice as a souvenir.

The students, from time immemorial, had a voluntary organisation to maintain order in the laboratory; they elected at the beginning of each semester an officer known as "*Polizei-Diener*," who was authorised to impose small fines for petty offences, the money thus secured being devoted at the end of the term to the purchase of books for the small library placed on shelves in the balance-room. This custom I understand still obtains. At the opening of my third term I was elected "*Polizei*," and duly instructed in my duties; being watchful and courageous I collected more money during my term of office than had been added to the library fund for many years. The misdemeanours for which fines were imposed were:—Leaving an unused gasburner lighted, failure to resort to the "*Stink-Zimmer*" when noxious gases were generated, failure to replace bottles or apparatus used in common, and leaving a balance door open or weights on the pans, which latter was accounted a very heinous offence; the fines ranged from six kreutzers (Baden) to half a gulden. My official life was marked by two events that greatly excited and amused the whole laboratory; one of the events was regarded as an exhibition of unparalleled audacity, of which only an American was capable—I fined Hofrath Bunsen! The Professor, after lighting his cigar at the flame of a Bunsen burner, left the gas burning and went out of the room; according to custom, and to the consternation of the students, I chalked on the desk that Bunsen had used, the words "six Kr." over my initials, a notice that could not be erased until the fine was paid. Next day when Bunsen approached the desk, he glanced at the inscription, smiled broadly, and, to the amusement of the crowd of students that had gathered to see the result of my daring, opened his purse and handed me the six kreutzers with a pleasant commendation of the fidelity of the "*Polizei*."

The other event concerned a very close-fisted American whose numerous fines I was unable to collect; when they reached the enormous sum of one and a half gulden (about 2s. 5d.), I consulted some of the older German students, stating the facts and asking for advice. They declared they had never heard of such a case, and they authorised me to confiscate some chemical apparatus belonging to the American and to sell it at auction. I secured a fine beaker glass, the outside one of a large nest, and after due notice, amid the shouts of the fifty-nine students gathered in the lecture-room, the beaker was sold at auction; the competition to secure it was so keen that it brought a very high price, the sum covering the fine plus

the value of the glass. The excess had to be paid back to the lucky American, so that the fine did not come out of his pockets after all.

Several times in the course of his life Bunsen was injured by explosions; he was popularly believed to be minus one eye, one ear, and one lung, and there is some foundation for this, for he lost an eye when working at cacodylate, and he was slightly deaf. It was related of him that on one occasion a violent explosion threw him to the ground and made him unconscious; on coming to, his first words were: "Has any of the substance been saved?"

In 1865 Bunsen was invited to fill a chair in the University of Berlin, and after due consideration he declined the flattering call, to the delight of all educational Heidelberg. In his honour the students organised a torchlight parade; the chemists marched in a body, and carried away by enthusiasm I imprudently joined them, carrying a torch with the crowd. The procession paraded the principal streets, and then assembled in the open square before the *Aula* or central Hall of the University; there the students singing the Studenten Lieder and formed a ring, gradually closed in towards the centre, making the ring smaller, until at a given signal they threw their half-burned torches into the very centre and the pile blazed on high, making an impressive ceremonial. I have said I imprudently joined because I failed to anticipate the disagreeable consequences; the smoke of a half-a-thousand torches, the dripping grease, and the dust of the streets, combined with the moist exudation of my membranous integument, to form a black deposit that would have honoured a stoker, besides ruining a suit of clothes.

During my residence in Heidelberg a lamentable and terrible affair took place that threw a profound gloom over the University and the entire town. Two German students having quarrelled decided the earth was not large enough for both of them to live in, and resorted to the diabolical practice called the "American Duel." In a darkened room the two young men drew lots, having sworn that he who drew the black ball would commit suicide. The unhappy loser went to his room and discharged a bullet into his breast, but missed his heart and lingered for several days on his death-bed; his parents were summoned by telegraph, and besought him on their knees to disclose the name of his antagonist, but he steadfastly refused and died with the secret in his breast. The students not only excused his conduct, but praised his courage, and when his remains were taken to the railway-station to be transported to a distant city, they accompanied the funeral cortège with torches and music. The students claimed he was not a suicide, for he was killed in an honourable duel, and they maintained that his opponent was not accessory to his death because he shot himself: I had many arguments with them, and never could convince them of their extraordinary tergiversation.

The whole system of duelling at Heidelberg is an interesting feature of student life that I had good opportunities of observing without taking part, but, as Kipling says, "that is another story."

The intimacy of Bunsen and Kopp is well known; I have often seen them walk through the narrow streets hand-in-hand like affectionate school-girls, Bunsen's large frame and Kopp's diminutive stature making a strong contrast.

Bunsen had great talents and personal attractions, yet he did not succeed in fostering original work on the part of those who studied with him; I think this is partly due to the fact they were chiefly beginners, and when they had acquired the rudiments of general chemistry they took to the fertile fields of organic chemistry under other masters. Yet his pupils include some men of high rank in the profession—Lothar Meyer, Sir Henry Roscoe, Beilstein, Lieben, and Carius.

I last saw Geheimerath Bunsen during a brief visit to Heidelberg in 1891; he had retired from active duty and complained of the infirmities of advancing years, being subject to rheumatism; but he exhibited the same cordial

manner, the charming smile, and a willingness to listen to the accounts of Americans who had pursued their studies in the Heidelberg Laboratory. Bunsen died after a lingering illness, August 16th, 1899, at the great age of 88.

Of the charm of residence in the picturesque little city on the Neckar, with its magnificent ruined castle, its attractive forest-covered hills threaded by enticing paths, its historical associations, and its excellent beer, there can be but one opinion; but in winter we often felt the truth of the old couplet:—

"Heidelberg ist eine schöne Stadt
Wenn es ausgereget hat!"

SEPARATION OF IRON FROM CHROMIUM, ZIRCONIUM, AND BERYLLIUM BY THE ACTION OF GASEOUS HYDROCHLORIC ACID ON THE OXIDES.*

By FRANKE STUART HAVENS and ARTHUR FITCH WAY.

It has been shown in a former paper from this laboratory (Gooch and Havens, *Am. Journ. Sci.*, vol. viii., No. 41, May, 1899; *CHEMICAL NEWS*, vol. lxxx., p. 39) that iron oxide may be completely volatilised as chloride by a strong current of hydrochloric acid gas acting at a temperature of 450–500°, and also that the addition of a little free chlorine to the gaseous hydrochloric acid renders this action complete at lower temperatures (180–200°) without the danger of error arising from the liability of ferric chloride to dissociation, or from deficiency of oxidation in the oxide treated, or mechanical loss due to too rapid volatilisation. It has also been shown that this reaction can be employed for the separation of iron and aluminum, taken as the oxides, and its application to the separation of iron from other metallic oxides has been suggested.

The oxides of chromium, zirconium, and beryllium, like aluminum oxide, are not acted upon by a current of dry hydrochloric acid gas at the temperatures before mentioned, and these oxides also can be entirely freed from iron by this reaction, as the experiments to be described will show. The procedure was the same in each case and analogous to that employed for the separation of iron from aluminum. A mixture of a weighed portion of one of these oxides with a weighed portion of ferric oxide, contained in a porcelain boat and placed within a roomy glass tube supported in a small combustion furnace, was submitted to the action of a dry current of hydrochloric acid gas and chlorine generated by dropping sulphuric acid upon a mixture of strong hydrochloric acid, common salt, and a small amount of manganese dioxide. The gas was admitted at one end of the combustion tube and passed out at the other through a water trap, while the required temperature (from 200–300°) was maintained by regulating the various burners of the furnace. The time of action varies somewhat with the condition of the oxide to be volatilised, and the temperature, generally an hour's heating at 200°, proves sufficient for the complete removal of 0.1 grm. of iron. At higher temperatures the action is more rapid; but the lighter oxide, the beryllium especially, is liable to mechanical loss through the too rapid volatilisation of the iron, as Experiment 17, where a temperature of 500° was used, will show. It is better, therefore, to use lower temperatures, raising the heat for a few minutes when the action is apparently complete to ensure the removal of the last traces of iron. Tests showed the residual oxides from which the ferric oxides had been removed in this manner to be entirely free from iron.

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. viii., September, 1899.

Expt.	Fe ₂ O ₃ taken. Grm.	Cr ₂ O ₃ taken. Grm.	Cr ₂ O ₃ found. Grm.	Error. Grm.
1	—	0.1008	0.1008	0.0000
2	0.1007	0.1006	0.1006	0.0000
3	0.1007	0.1000	0.1002	+0.0002
4	0.1010	0.1005	0.1003	-0.0002
5	0.1019	0.1006	0.1005	-0.0001
6	0.2007	0.1003	0.0999	-0.0004
ZrO ₂ taken. ZrO ₂ found.				
7	—	0.1516	0.1516	0.0000
8	0.1053	0.1010	0.1010	0.0000
9	0.1204	0.1519	0.1523	+0.0004
10	0.1236	0.1516	0.1517	+0.0001
11	0.2150	0.1517	0.1519	+0.0002
BeO taken. BeO found.				
12	—	0.1309	0.1311	+0.0002
13	—	0.1285	0.1285	0.0000
14	0.0997	0.0456	0.0457	+0.0001
15	0.1045	0.1099	0.1099	0.0000
16	0.1215	0.1080	0.1081	+0.0001
17	0.1510	0.1305	0.1290	-0.0015
18	0.2030	0.1081	0.1083	+0.0002

The separation of iron from chromium, zirconium, and beryllium by this method is obviously complete within very satisfactory limits of error.

ON THE ESTIMATION OF THALLIUM AS THE CHROMATE.*

By PHILIP E. BROWNING and GEORGE P. HUTCHINS.

CROOKES has shown (CHEM. NEWS, viii., 255) that the chromate precipitated by the addition of potassium dichromate to an alkaline solution of a thallous salt has the constitution of a neutral salt and is very insoluble in water—100 parts of water at 100° C. dissolving about 0.2 part, and at 60° C. about 0.03 part. He has also made use of this reaction (CHEM. NEWS, vii., 145) to effect a rough separation of thallium from cadmium.

The object of this paper is to describe some work directed toward a study of the application of this reaction to the gravimetric estimation of thallium and the best conditions under which to effect the precipitation. For the work, a solution of thallous nitrate was made by dissolving 10 grms. in water, making up to a litre. The standard was determined by taking measured and weighed portions from a burette, precipitating with a slight excess of potassium iodide, agitating to bring about a good separation of the thallous iodide, and allowing to stand until the supernatant liquid was clear. The iodide was then filtered off upon an asbestos felt contained in a perforated platinum crucible, the whole having been previously ignited and weighed, washed with a mixture of alcohol and water, dried over a low flame, and weighed to a constant weight. The filtrate, which together with the washings seldom amounted to more than 50 c.m.³, was evaporated to dryness on a water-bath, a few drops of water added, and thus the small amount of thallous iodide which had been dissolved recovered. This small insoluble residue, which seldom amounted to 1 m.grm. in weight, was filtered off, washed, and weighed as previously described. Baubigny (CHEM. NEWS, lxiv., 239) has shown this method to give very satisfactory results, and the uniformity of our determinations certainly confirms his statements.

For convenience in the calculations of results to be described later, a solution of potassium dichromate of definite strength was made. Portions of the thallium

solution were drawn from a burette into test-tubes of about 100 c.m.³ capacity, and weighed as a check on the burette reading. The solution was heated to about 70° C. to 80° C., and a few drops of ammonia or potassium carbonate solution added to distinct alkalinity. A definite amount of the potassium dichromate in solution was delivered from a burette, care being taken to have an excess, and the contents agitated to bring about a good separation of the precipitated chromate. After the precipitate had completely settled out and the solution had become cold, the chromate was filtered upon asbestos, as described above, dried over a low flame, and weighed to a constant weight. The filtrates from several determinations were evaporated to a small volume, and in one or two cases a residue amounting to a few tenths of a milligram. was obtained, but no appreciable quantity of dissolved chromate was thus recovered. It was found that when the precipitation was made in the cold the chromate did not flock well, but remained partly in a finely-divided condition which would run through the felt and require repeated filtration. The addition of ammonium nitrate before precipitation prevented this largely, even in the cold, but the best results were obtained by warming the solution before precipitation, and using potassium carbonate rather than ammonium hydroxide. The results follow in Table I.

TABLE I.

	TlNO ₃ taken. Calculated as Tl ₂ O. Grm.	Tl ₂ CrO ₄ found. Calculated as Tl ₂ O. Grm.	Error. Calculated as Tl ₂ O. Grm.
1.	0.0796	0.0791	0.0005—
2.	0.0792	0.0788	0.0004—
3.	0.0792	0.0786	0.0006—
4.	0.1188	0.1177	0.0011—
5.	0.1192	0.1186	0.0006—
6.	0.1185	0.1178	0.0007—
7.	0.1190	0.1185	0.0005—
8.	0.1189	0.1183	0.0006—
9.	0.1196	0.2000	0.0004+
10.	0.1196	0.2005	0.0009+
11.	0.1173	0.1173	0.0000
12.	0.1171	0.1163	0.0008—

An attempt was made to estimate the thallium volumetrically by determining the amount of chromate in the filtrate from the thallous chromate, and by difference (the potassium dichromate originally added being known) the amount combined with the thallium in the precipitate. The method used to determine the standard of the dichromate solutions and also the chromate remaining in the filtrate was described by one of us in a previous paper from this laboratory (*Am. Journ. Sci.*, 1896, vol. i., 35). According to this procedure, the filtrate from the thallous chromate containing the excess of alkali chromate was acidified with sulphuric acid, a definite amount of a solution of arsenious oxide (previously standardised) was added, and the whole was allowed to stand a few moments until the change from the yellow to the bluish green showed the complete reduction of the chromic acid. Potassium bicarbonate was added to distinct alkaline reaction, and the arsenious oxide remaining was determined by titration with standard iodine solution. The amount of the arsenious oxide oxidised is, of course, the measure of the chromate in the solution. The amount of chromate in the original solution used being known, by subtracting

TABLE II.

	TlNO ₃ taken. Calculated as Tl ₂ O. Grm.	Tl ₂ CrO ₄ found. Calculated as Tl ₂ O. Grm.	Error. Calculated as Tl ₂ O. Grm.
5.	0.1192	0.1198	0.0006+
8.	0.1189	0.1205	0.0016+
9.	0.1195	0.1180	0.0016—
10.	0.1196	0.1192	0.0004—
11.	0.1173	0.1182	0.0009+
12.	0.1171	0.1190	0.0019+

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, viii., No. 48, 1899.

the amount thus determined in the filtrate, the chromate in combination with the thallium may be readily found, and from it the thallium estimated. Filtrates from certain precipitates of which the determinations are given in Table I. were treated in this way, and the results (indicated by corresponding numbers) follow in Table II.

The method cannot be very accurate on account of the high molecular weight of thallium oxide as compared with that of the chromic acid determined, but the results check fairly well with the gravimetric method.

MEMOIR OF THE LATE WILLIAM JOHN COCK.

WILLIAM JOHN COCK, the subject of this memoir, was born on the 8th January, 1813, near Hemel Hempstead, in Hertfordshire. His father, Mr. Thomas Cock, was a very able chemist, and was of great service to his brother-in-law, Mr. Percival Johnson, founder of the well-known firm of Johnson, Matthey, and Co., Hatton Garden, London, in the preparation of colours for china painting, &c.

In the year 1834 William John Cock entered, under indentures of apprenticeship, the business then carried on by his uncle, under the name of Johnson and Stokes, as assayer and refiner; after having thoroughly mastered the business, and being in charge of the gold refinery, he was, in 1837, taken into partnership, the business then being carried on under the style of Johnson and Cock. He very soon effected important improvements, and his arrangement of sand baths is in use at the Hatton Garden works to this day. He also made many other important alterations and improvements in gold refining, and the recovery of silver from the refining solutions; he also organised the plant for producing uranium oxide from the mineral pitchblende.

It was, however, in dealing with the minerals of the platinum group that Mr. Cock most distinguished himself, and at one time he had no equal in the knowledge of the treatment of the metals, platinum, iridium, rhodium, and palladium. His ability and resources are said to have been almost endless, and he has been known to work for days together, hardly ever speaking, from 7 a.m. to midnight, with perhaps half an hour for a meal.

He was a first rate theoretical chemist, an excellent mechanic and carpenter, there being hardly a tool he could not handle.

In 1845, owing to a temporary failure in health, he retired from the partnership, but in the year 1849, being unable to remain idle, he returned to Hatton Garden and resumed charge of the uranium oxide manufacture.

In 1852, his health again failing, he determined to go for a sea voyage to Australia, the gold fever being then at its height, but he only remained three weeks ashore, and returned to England, when in 1853 he again went back to Hatton Garden, and this time took entire charge of the platinum refinery. Here, as usual, he effected many improvements, and always conducted the forging of the platinum ingots himself; he was in fact the first to work on large ingots of 500 and 1000 ozs. instead of the old-fashioned smaller ones.

Mr. W. J. Cock left Hatton Garden for the last time in the year 1861, and after another sea voyage, this time to New Zealand, whence he returned the following year, he finally gave up work and went to live in the country. He never married, though he was a universal favourite with both old and young. He died in December, 1892, at Ashburton, at the age of 79.

Owing to his somewhat retiring habits, his wonderful ability has not become as widely known as it should have been; if he had put himself more forward he would undoubtedly have obtained honour and distinction in the scientific world, but all his ambition seemed to be to properly complete the work he had in hand. To some

this life would seem uneventful, but those who knew him appreciate how much our country, with its vast metallurgical interests, owes to him.

A NEW VOLUMETRIC METHOD FOR MAGNESIUM.*

By RICHARD K. MEADE.

(Concluded from p. 276).

THE next, and the method finally adopted as the one most suited to the volumetric determination of magnesium, was the one worked out by A. Williamson and described by him in the *Journal of the Society of Dyers and Colourists*, May, 1896. A description of the method is also to be found in Sutton's "Volumetric Analysis," p. 369.

It depends, like the method of Gooch and Browning, upon the reaction between arsenic acid and potassium iodide. Williamson found that where a solution of arsenic acid contained sufficient sulphuric or hydrochloric acid the arsenic is quickly reduced from the higher to the lower state of oxidation, even in the cold, according to the reaction $\text{As}_2\text{O}_5 + 4\text{KI} + 4\text{HCl} = \text{As}_2\text{O}_3 + 4\text{KCl} + 2\text{H}_2\text{O} + 2\text{I}_2$. For every molecule of arsenic acid reduced, corresponding to two atoms of magnesium, two molecules or four atoms of iodine are liberated. This latter is titrated with sodium thiosulphate, and from the amount of standard solution required the magnesium calculated.

The process followed consisted in dissolving the precipitated magnesium-ammonium arsenate in dilute hydrochloric acid, washing the filter-paper well with the acid, and—after adding potassium iodide and allowing to stand for a few minutes—titrating with standard thiosulphate. This latter corresponded, c.c. for c.c., with the iodine solution mentioned above. Below are the results:—

No.	Stock solution taken.	Equivalent to MgO.	"Hypo" required.	Equivalent to MgO.
	C.c.	Grm.	C.c.	Grm.
1	50	0.2495	49.8	0.2490
2	50	0.2495	49.9	0.2495
3	25	0.1247	25.0	0.1250
4	25	0.1247	24.9	0.1245
5	10	0.0499	9.95	0.0498
6	5	0.0249	5.0	0.0250

Determinations required only from seven to ten minutes by this method after the arsenic was in solution, and were just as accurate as those by the longer method of digestion with potassium iodide.

The attempt was next made with success to hasten the precipitation of the magnesium by violent agitation. Fifty c.c. of the stock solution were measured into a large Erlenmeyer flask, diluted to about 500 c.c., and one-third this volume of strong ammonia and 50 c.c. of a 10 per cent solution of sodium arsenate added, the flask corked up tightly and shaken violently by hand for ten minutes. After allowing the precipitate to settle, it was filtered, and the arsenic determined as described above.

No.	Stock solution taken.	Equivalent to MgO.	"Hypo" required.	Equivalent to MgO.
	C.c.	Grm.	C.c.	Grm.
1	50	0.2495	49.9	0.2495
2	50	0.2495	49.9	0.2495
3	25	0.1247	24.8	0.1240
4	15	0.0748	15.0	0.0750
5	10	0.0499	9.9	0.04950
6	5	0.0249	4.9	0.0245

The time required for the precipitation, filtration,

* Read before the Lehigh Valley Section of the American Chemical Society, May 16, 1899. From the *Journal of the American Chemical Society*, vol. xxi., No. 9, September, 1899.

washing, re-solution, and titration had now been shortened to about three-quarters of an hour.

The standard thiosulphate was titrated against standard sodium arsenate, prepared by dissolving 12.29 grms. of pure arsenious acid in nitric acid, evaporating to dryness on a water-bath, neutralising with sodium carbonate, and diluting to one litre. Each c.c. of this solution was equivalent to 0.005 grm. of magnesium oxide. The values obtained by titration of the standard thiosulphate against this solution coincided with those obtained by titration with standard iodine solution. The values obtained by titration against standard bichromate and potassium iodide did not differ materially from those obtained by titration against standard arsenate or standard iodine.

The method finally worked out is as follows:—

Pour the solution, which should not contain too great an excess of ammonium chloride or ammonium oxalate into a large Erlenmeyer flask or a gas-bottle of sufficient capacity. Add one third the volume of the solution of strong ammonia and 50 c.c. of sodium arsenate. Cork up tightly and shake vigorously for ten minutes. Allow the precipitate to settle somewhat, and wash with a mixture of three parts water and one part strong ammonia until the washings cease to react for arsenic; avoid using an excess of the washing fluid, however. Dissolve the precipitate in dilute hydrochloric acid (1:1), allowing the acid solution to run into the flask in which the precipitation was made, and wash the filter-paper with the dilute acid, until the washings and solution measure 75 or 100 c.c. Cool, if not already so, and add from 3 to 5 grms. of potassium iodide, free from iodate; allow the solution to stand a few minutes, and then run in the standard thiosulphate until the colour of the liberated iodine fades to a pale straw colour. Add starch, and titrate until the blue colour of the iodide of starch is discharged. If preferred, an excess of thiosulphate may be added, then starch and standard iodine until the blue colour is produced. On adding the iodide of potassium to the acid solution, a brown precipitate forms, which, however, dissolves when the thiosulphate is added.

Below are some results upon the method as given above:—

Sample.	MgO.		Thiosulphate required.	MgO.	
	Gravimetric.	Per cent.		Volumetric.	Per cent.
Dolomite	21.78		43.3	21.65	
			43.4	21.70	
Limestone	9.16		18.2	9.10	
			18.2	9.10	
Slag	16.42		32.6	16.30	
			32.5	16.25	
Cement, Portland ..	2.57		5.1	2.55	
Cement, Natural..	11.03		22.0	11.00	
			22.2	11.10	

PICTURES PRODUCED ON PHOTOGRAPHIC PLATES IN THE DARK.*

By WILLIAM JAMES RUSSELL, Ph.D., V.P.R.S.

I THINK I may fairly assume that every one in this theatre has had their photograph taken, and consequently must have some idea of the nature of the process employed. I have, therefore, only to add, with regard to what is not visible in the process of taking the picture, that the photographic plate is a piece of glass or such like body, coated on one side by an adhesive paste which is acted on by light, and acted on in a very remarkable manner. No visible change is produced, and the picture might remain latent for years, but place this acted-on plate in a solution of, say, pyrogallol, and the picture appears. The subsequent treatment of the plate with

sodium hyposulphite is for another purpose, simply to prevent the continuance of the action when the plate is brought into the light. Now, what I purpose demonstrating to you to-night is that there are other ways of producing pictures on photographic plates than by acting on them by light, and that by these other means a latent picture is formed, which is rendered visible in precisely the same way as the light pictures are.

The substances which produce on a photographic plate these results so strongly resembling those produced by light, are, some of them, metallic, while others are of vegetable origin. At first it seemed very remarkable that bodies so different in character should act in the same way on the photographic plate. The following metals—magnesium, cadmium, zinc, nickel, aluminium, lead, bismuth, tin, cobalt, antimony—are all capable of acting on a photographic plate. Magnesium most strongly, antimony but feebly, and other metals can also act in the same way, but only to a very slight extent. The action in general is much slower than that of light, but under favourable conditions a picture may be produced in two or three seconds.

Zinc is nearly as active as magnesium or cadmium, and is the most convenient metal to experiment with. In its ordinary dull state it is without the power of acting on a photographic plate, but scratch it or scrape it, and it is easy to prove that the bright metal is active. I would say that all the pictures which I have to show you, by means of the lantern, are produced by the direct action of the metal, or whatever the active body may be, on the photographic plate, and that they have not been intensified or touched up in any way. This first slide is the picture given by a piece of ordinary zinc which has been rubbed with some coarse sand-paper, and you see the picture of every scratch. Here is a piece of dull zinc on which some circles have been turned. It was exposed to the photographic plate for four hours at a temperature of 55° C. In the other cases, which are on a larger scale, a zinc stencil was polished and laid upon a photographic plate, and you see where the zinc was in contact with the plate much action has occurred. In another case a bright zinc plate was used, and a Japanese stencil interposed between it and the photographic plate, and a very strong and sharp picture is the result. The time required to produce these zinc pictures varies very much with the temperature. At ordinary temperature the exposure would have to be for about two days, but if the temperature was, say, 55° C., then half to three-quarters of an hour might be sufficient. Temperatures higher than this cannot be used except for very short times, as the photographic plate would be damaged. Contact between the zinc and photographic plate is not necessary, as the action readily takes place through considerable distances. Obviously, however, as you increase the distance between object and plate, so you decrease the sharpness of the picture, as is shown by the following pictures, which were taken respectively at a distance of 1 mm. and 3 m.m. from the scratched zinc surface. The appearance of the surfaces of different metals varies, and the following slides show the surface of a plate of bismuth, a plate of lead, and one of aluminium. On the next slide are the pictures produced by similar pieces of pure nickel and cobalt, and it clearly shows how much more active in this way nickel is than cobalt. Many alloys, such as pewter, fusible metal, brass, &c., are active bodies, and in the case of brass the amount of action which occurs is determined by the amount of zinc present. Thus you will see that a brass with 30 per cent of zinc produces hardly any action on the photographic plate, but when 50 per cent of zinc is present there is a fairly dark picture, and when as much as 70 per cent is present a still darker picture is produced.

The second class of bodies which act in the same way on a photographic plate are organic substances, and belong essentially to the groups of bodies known as terpenes. In trying to stop the action of metallic zinc,

* A Lecture delivered before the Royal Institution of Great Britain, May 5, 1899.

which I thought at the time might arise from vapour given off by the metal, copal varnish was used, but in place of stopping the action it was found to increase it, and this increase of activity was traced to the turpentine contained in the varnish. In experimenting with liquids it is convenient to use small shallow circular glass vessels such as are made for bacteriological experiments, the plate resting on the top of the vessel, and the amount of liquid in the vessel determining the distance through which the action shall take place. The following slide, produced in this way, shows how dark a picture ordinary turpentine produces. All the terpenes are active bodies. Dipentene is remarkably so; in a very short time it gives a black picture, and if the action be continued, the dark picture passes away, and you then have a phenomenon corresponding to what photographers call reversal. The strong smelling bodies known as essential oils, such as oil of bergamot, oil of lavender, oil of peppermint, oil of lemons, &c., are all active bodies, and all are known to contain in varying quantities different terpenes; therefore ordinary scents are active bodies, and this is shown by the following pictures produced by Eau de Cologne, by cinnamon, by coffee, and by tea. Certain wines also act in the same way: Sauterne gives a tolerably dark picture, but brandy only a faint one. Other oils than these essential ones are also active bodies: linseed oil is especially so; olive oil is active, but not nearly as much so as linseed oil; and mineral oils, such as paraffin oil, are without action on the photographic plate.

Interesting results are obtained with bodies which contain some of these active substances; for instance, wood will give its own picture, as is shown by the following slides: the first is a section of a young spruce tree, the next a piece of ordinary deal, and the third of an old piece of mahogany. Again, the next slide you will recognise as the picture of a peacock's feather. There is much interest in these pictures of feathers, as they distinguish the brilliant interference colours from those produced by certain pigments; the beautiful blue in the eye of the peacock's feather is without action on the photographic plate. Butterflies' wings, at least some of them, will draw, as you see, their own pictures. Linseed oil, which is a constituent of all printing ink, makes it an active body, and it can, like the zinc and other active bodies, act through considerable distances. In the picture before you the ink was at a distance of one inch from the plate, and the next slide shows what a remarkably clear and dark picture ordinary printing can produce. As the composition of printing ink varies so does its activity, and here are pieces of three different newspapers which have acted under the same conditions on the same plate, and you see how different the pictures are in intensity. Printed pictures, of course, act in the same way—here is a likeness of Sir H. Tate, taken from "The Year's Art." The pictures and printing in *Punch* always print well, so does the yellow ticket for the Friday evening lectures at the Royal Institution; also the rude trade-mark on Wills's tobacco, and it is of interest because the red pigment produces a very clear picture, but the blue printing is without action on the plate.

An interesting and important peculiarity of all these actions is that it is able to pass through certain media; for instance, through a thin sheet of gelatin. Here are two plates of zinc; both have been scratched by sand-paper; one is laid directly on the photographic plate, and the other one has a sheet of gelatin, its colour is of no note, laid between it and the sensitive plate; the picture in this case is, of course, not so sharp as when no gelatin is present, but it is a good and clear likeness of the scratches.

Celluloid is also a body which allows the action to pass through it, as is seen in this picture of a piece of perforated zinc, a picture which was produced at ordinary temperatures. Gold-beaters' skin, albumen, collodion, gutta-percha, are also bodies which are transparent to the action of the zinc and the other active bodies. On the

other hand, many bodies do not allow the transmission of the action through them; for instance, paraffin does not, and among common substances writing ink does not, as is easily shown by placing ordinary paper with writing on it between the active body and the photographic plate. The active body may conveniently be either a plate of zinc or a card painted with copal varnish and allowed to dry, or a dish of drying oil. The picture of an ordinarily directed envelope shows this opacity of ink well. It is a property long retained by the ink, as this picture of the direction of a letter, written in 1801, shows; also this letter of Dr. Priestley's, dated 1795; and here is also some very faded writing of 1810, which still gives a very good and clear picture. Even if the writing be on parchment, the action passes through the parchment, but not through the ink, and hence a picture is formed.

With bodies which are porous, such as most papers, for instance, the action passes gradually through the interstices, and impresses the plate with a picture of the general structure of the intervening substance. For instance, the following pictures show the structure and the water-mark of certain old and modern writing-papers. Some modern writing papers are, however, quite opaque; but usually paper allows the action to take place through it, and combining this fact with the fact of strong activity of the printing ink, the apparently confused appearance produced on obtaining a picture from paper with printing on both sides is accounted for, as the printing on the side away from the photographic plate, as well as that next to it, prints through the paper, and is, of course, reversed.

I hope I have now given you a clear idea how a picture can be produced on a photographic plate in the dark, and the general character and appearance of such pictures. I now pass on to the important question of how they are produced. Moser suggested 50 years ago that there was "dark light," which gave rise to pictures on polished metallic plates, and lately it was suggested that pictures were produced by vapour given off by the metals themselves; the explanation, however, which I have to offer you is, I think, simpler than either of these views, for I believe that the action on the photographic plate is due to the formation of a well-known chemical compound, hydrogen peroxide, which undergoing decomposition acts upon the plate and is the immediate cause of the pictures formed. The complicated changes which take place on the sensitive plate I have nothing to say about on the present occasion, but I desire to convince you, that this body, hydrogen peroxide, is the direct cause of these pictures produced in the dark. Indirect proof has to be resorted to. Water cannot be entirely excluded, for an absolutely dry photographic plate would probably be perfectly inactive, and as long as water is present peroxide of hydrogen may be there also. But what are the conditions under which these pictures are formed? Only certain metals are capable of producing them. This list of active metals which I have mentioned to you was determined solely by experiment, and when completed it was not evident what common property bound them together. Now, however, the explanation has come, for these are the very metals which most readily cause, when exposed to air and moisture, the formation of this body, peroxide of hydrogen. Schönbein showed, as long ago as 1860, that when zinc turnings were shaken up in a bottle with a little water, hydrogen peroxide was formed, and the delicate tests which we now know for this body show that all the metals I named to you not only can in the presence of moisture produce it, but that their power of doing so follows the same order as their power of acting on a photographic plate. Again, what happened with regard to the organic bodies which act on the photographic plates? I have already mentioned that in experimenting with the metals it was accidentally observed that copal varnish was an active substance producing a picture like that produced by zinc, and that the action was traced to the turpentine present; again a process very much like groping in the dark had to be carried on in order to deter-

mine which were active and which inactive organic bodies, and the result obtained was that the active substances essentially belonged to the class of bodies known to chemists as terpenes. Now a most characteristic property of this class of bodies is that in presence of moisture and air they cause the formation of hydrogen peroxide, so that whether a metal or an organic body be used to produce a picture, it is in both cases a body capable, under the circumstances, of causing the formation of hydrogen peroxide. Passing now to experimental facts, which confirm this view of the action on sensitive plates, I may at once say that every result obtained by a metal or by an organic body can be exactly imitated by using the peroxide itself. It is a body now made in considerable quantity, and sold in solution in water. Even when in a very dilute condition it is extremely active. One part of the peroxide diluted with a million parts of water is capable of giving a picture. It can, of course, be used in the glass dishes like any other liquid, but it is often convenient not to have so much water present; and then it is best to take white blotting-paper, wet it in the solution of the peroxide, and let it dry in the air. The paper remains active for about twenty-four hours; or, what is still better, take ordinary plaster of Paris, wet it with the peroxide solution, and let it set "in a mould" so as to get a slab of it. This slab increases in activity for the first day or two after making, and retains its activity for a fortnight or more. Such a slab will give a good and dark picture in three or four seconds.

To show how similar the pictures produced by the peroxide and those by zinc are, pictures of a Japanese paper stencil, which had been paraffined to make it quite opaque, have been made by both processes, and are shown with other instances in which turpentine was used in the following slides. It is also very easy to obtain good pictures with the peroxide alone of the structure of paper, &c.; see, for instance, this one of a five-pound note and these of lace. Again, the strict similarity between the action of the peroxide and that of the metals and organic bodies is further shown by the fact that its action passes through the same media as their action does; and here are good pictures formed by the action of the peroxide after passing through a sheet of these substances. How this singular transmission can be explained I have treated of elsewhere, and time does not allow of my discussing the matter to-night.

There are many ways in which the bright active zinc surface can be modified. Draw your finger across it, press your thumb upon it, and you stop its activity, as is shown by the picture it will give. Lay a printed paper on the zinc, and let the contact continue for three-quarters of an hour, at a temperature of 55° , then bring the zinc in contact with a sensitive plate, a picture of the printing is formed; but allow the contact between the zinc and printing to continue for eighteen hours at the same temperature, and the picture then given by the zinc is the reverse of the former one. Where the ink has been is now less active than the rest of the plate. Here are slides which show these positive and negative pictures. Another way of modifying the zinc surface is interesting. You have seen that the ordinary zinc surface which has been exposed to air and moisture is quite inactive, but if a bright piece of zinc be immersed in water for about twelve hours the surface is acted on; oxide of zinc is formed, showing generally a curious pattern. Now, if the plate be dried, it will be found that this oxide is strongly active, and gives a good picture of the markings on the zinc. The oxide evidently holds, feebly combined or entangled in it, a considerable quantity of the hydrogen peroxide, and it requires long drying or heating to a higher temperature to get rid of it. Also, if a zinc plate be attacked by the hydrogen peroxide, the attacked parts become more active than the bright metal. Thus place a stencil on a piece of bright zinc, and expose the plate to the action of an active plaster of Paris slab, or to active blotting-paper for a short

time, then, on removing the stencil, the zinc plate will give a very good picture of the stencil. Any inactive body—for instance, a piece of Bristol board or any ordinary soft paper—can be made active by exposing it above a solution of peroxide, or, more slowly, by exposing it to a bright zinc surface. If, for instance, a copper stencil be laid on a piece of Bristol board, and a slab of active plaster of Paris be placed on the stencil for a short time, the Bristol board will even, after it has been removed from the stencil for some time, give a good picture of the stencil. Drying oil and other organic bodies may be used in the same way to change the paper. A curious case of this occurred in printing a coloured advertisement cut out of a magazine, for there appeared printing in the picture which was not in the original. This printing was traced to an advertisement on the opposite page, which had been in contact with the one which was used; thus this ghostly effect was produced.

I believe, then, that it is this active body, hydrogen peroxide, which enables us to produce pictures on a photographic plate in the dark. There are many other curious and interesting effects which it can produce, and which I should like to have shown you, had time permitted.

I would only add that this investigation has been carried on in the Davy-Faraday Laboratory of this Institution.

Radio-active Effect of Barium Salts and Polonium.—In the course of a paper on these subjects, F. Giesel (*Wied. Ann.*, No. 9, 1899, p. 91), the author, states that a surprising difference exists in regard to the penetrating power of the rays of radium and those of polonium. While the rays from radium penetrate fairly well a silver thaler, the rays from polonium, although more intense, are absorbed by thinner metallic plates. The shadow of the hand and of metallic objects thrown by the polonium rays on a fluorescent screen are stronger in contrast than when produced by the radium rays.—*American Journal of Science*, viii., No. 48.

Magnetising Constants of Inorganic Substances.—Stefan Meyer (*Wied. Ann.*, No. 9, 1899, p. 236) has made an extended study of the behaviour of a large number of inorganic substances in the magnetic field, and gives tabulated results. One of the most interesting facts he states is in regard to erbium. In the combination Er_2O_3 it is four times stronger than Fe_2O_3 . If in the pure metallic state it were as magnetic as it is in the state of oxide, one could reduce the weight of dynamos one-sixth and still obtain the same output as when iron is employed.—*American Journal of Science*, viii., No. 48.

Dispersion of the Cathode Rays by Magnetic Force.—M. Birkeland (*Phil. Mag.*, Nov., 1899, p. 478) has observed that when a narrow beam of cathode rays produced by an induction coil is deflected by a magnetic field, that certain rays are deflected more than others, and he has given to this effect the name of the magnetic spectrum. R. J. Strutt, of Trinity College, Cambridge, has examined this subject, and by the use of a storage battery of 800 cells shows that the formation of the magnetic spectrum is due to a peculiarity of the induction coil. The cathode rays produced by a battery are homogeneous.—*American Journal of Science*, vol. viii. No. 48, 1899.

Lavoisier's Monument.—At the last meeting of the Paris Academy of Sciences, M. Berthelot gave some details regarding the monument to Lavoisier, which is to be unveiled while the Paris Exhibition is open. M. Berthelot announced that a sum of 98,000 francs (nearly £4000) has been received in subscriptions, and the well-known sculptor Barrias has been entrusted with the work. The open space behind the Madeleine Church is the site selected.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, December 8th, 1899.

Prof. G. CAREY FOSTER, F.R.S., Vice-President, in the Chair.

By the invitation of Prof. S. P. Thompson, this meeting was held in the Physical Laboratory of the City and Guilds' Technical College, Finsbury.

Prof. S. P. THOMPSON read a paper "*On Obliquely-crossed Cylindrical Lenses.*"

Any two cylindrical lenses crossed obliquely are optically equivalent to two other cylindrical lenses crossed rectangularly, and hence to a spherocylindrical lens. Owing to the difficulty of manufacturing cylindrical lenses with the axes of the opposite faces in different directions it becomes of importance to the optician to be able to calculate the constants of the equivalent, but more easily ground, spherocylindrical lens. To a first approximation a surface of radius of curvature " r " will impress upon a plane wave a curvature of $\frac{\mu-1}{r}$ where " μ " is the re-

fractive index of the material. If we suppose an equiconvex cylindrical lens cut by two planes at right angles, the line of intersection of the planes passing normally through the centre of the lens, then the sections of the lens will in general be portions of ellipses. It is possible, therefore, to write down in terms of the angle which one of these planes makes with the axis the convergency which would be impressed by the lens upon plane waves travelling in these planes. The effect of a second lens crossing the first obliquely can also be written down with respect to the same two planes. The joint effect of the two lenses can then be resolved along any two lines at right angles. Differentiating the expressions for these effects and equating to zero, we get the directions of maximum and minimum cylindricity. These directions are at right angles and represent two lenses crossed rectangularly, which are the optical equivalent of the original pair considered. The spherocylindrical lens is then easily obtained. From the mathematical expressions Prof. Thompson has deduced a graphical solution of the problem. The author exhibited a convenient combination of two cylindrical lenses for giving varying degrees of cylindricity. Let two lenses be ground, each being a mixed equicylinder consisting of a concave and convex ground at right angles to one another on the opposite faces of the glass. Two such mixed cylinders, if rotated with equal motion in opposite directions, will give a varying cylindricity of fixed direction in space. With the axis of positive cylindricity coincident they give the maximum, but when each is rotated 45° their resultant is zero. When rotated beyond 45° the resultant axis of cylindricity is negative in the fixed direction in which it was formerly positive.

Mr. T. H. BLAKESLEY read a paper on "*Exact Formulæ for Lenses.*"

In this paper the author makes use of the definition of focal length with respect to magnifying power which he has described in the *Proceedings of the Physical Society* for November, 1897. By this method the focal length of a lens combination is simply a line, and not the distance between two definite points. Following the methods of his previous paper, Mr. Blakesley showed how it was possible to determine accurately the constants of lens combinations, and pointed out practical applications to the racking of telescopes for camera work, the determination of refractive indices of liquids, &c.

Prof. W. E. DALBY exhibited a Friction Dynamometer. The torque to be measured produces a twist in a spiral spring, and the object is to determine the amount of this

twist. Side by side upon the shaft are two pulleys, one keyed to the shaft, and the other fastened to the end of the spring. The lead of one pulley upon the other therefore measures the twist. Two other pulleys are mounted upon a slide, and are joined up to the first ones by means of a continuous band similar to a Weston's differential pulley block. When the shaft is at rest the two pulleys on the slide are touching, but any motion of the shaft produces a twist in the spring, and therefore a lead of one of the shaft pulleys on the other. This produces a separation of the slide pulleys which is proportional to the lead, and therefore to the torque, and so, from a knowledge of the constants of the dynamometer and its number of revolutions per second, the power transmitted is at once determined.

Prof. S. P. THOMPSON read a note "*On an Organic Compound of great Double Refraction.*"

This substance is crystallised naphthalene, and it is 60 per cent more doubly refracting than Iceland spar. It is exceedingly brittle, and therefore difficult to work into prisms. Any worked surface must be at once covered with glass to prevent sublimation.

The Society then adjourned until January 26th, 1900.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 21, November 20, 1899.

Action of Hydrofluoric Acid and Fluorine on Glass.—Henri Moissan.—In order to examine the action of hydrofluoric acid on glass, the author first decomposes dry fluorides by means of sulphuric acid. The hydrofluoric acid gas is rapidly produced, and remains gaseous at a temperature of $+20^\circ$, when the glass is immediately attacked. When Nordhausen sulphuric acid is used in the preparation of the acid, still the glass is attacked. Further experiments were also tried, but in all cases it was found that gaseous hydrofluoric acid attacks glass at ordinary temperatures, however carefully it was dried. Fluorine gas, obtained in a state of purity by freezing out the HF contained in it at a temperature of -92° and purifying it in every possible way, when placed in little glass bulbs and maintained at a temperature of 100° for some hours, does not attack the glass at all; but if a trace of moisture or a minute particle of organic matter is present, hydrofluoric acid is formed, and the glass attacked.

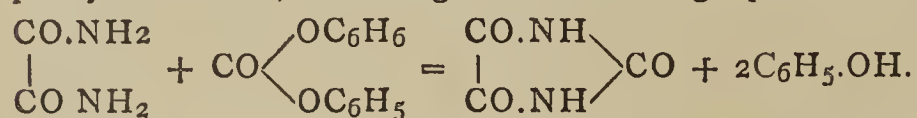
Chemical Effects produced by Becquerel Rays.—P. and Mme. Curie.—The rays emitted by radiferous salts of barium are very active, and are capable of transforming oxygen into ozone. The radiferous products necessary for the production of ozone are all very active and very luminous. The phenomenon appears to be more directly connected with radio-activity than with luminosity. It is found that very luminous radium carbonate produces less ozone than radium chloride, which is much less luminous, but more strongly radio-active. Again, if a radium salt is contained in a glass vessel, a violet colouration is seen in the glass, which proceeds from the interior to the exterior surface. At the end of ten days or so, the bottom of the flask is almost black. With a less active product, the tint is less deep and requires a longer time to produce. This phenomenon is not due to the reduction of lead, as it occurs in glass containing no lead. The effect of Becquerel rays on platinocyanide of barium is also a chemical effect. All these phenomena point to the fact that the rays emitted by radium represent a continual development of energy.

Reciprocal Displacement of Metals.—Alb. Colson.—The employment of Crookes's vacuum, and so the elimination of the perturbing influence of atmospheric oxygen and gases retained by solid bodies, enabled the author to establish the fact that the direct displacement of silver by mercury is, in certain cases, a reversible reaction limited by a tension of metallic vapour, as a heterogeneous dissociation is by a gaseous tension. Finally, this method of working shows that sulphide and oxide of cadmium are dissociable below 600°, and this fact is shown by the transparency of cadmium.

Action of Nitric Oxide on Chromic Dichlorhydrine.—V. Thomas.—When a current of nitrogen dioxide is passed into chlorochromic acid, a very vigorous action takes place. Large quantities of yellow coloured vapour are evolved, the temperature rises rapidly, and a black mass is formed, viscous for some time, and which is difficult to transform into a homogeneous solid product, even after the prolonged action of nitric oxide. After considerable trouble, the author obtained a brown powder acting readily on water, colouring it black. Analysis shows the formula $\text{Cr}_5\text{Cl}_5\text{O}_7 \cdot 2\text{NO}_2$ to express almost exactly the results of analysis:—Cr (total), 40.53; Cr (in state of chromic acid), 16.20; Cl, 27.66; N, 4.36. The substance is amorphous, and, on account of its easy decomposition, it is very difficult to purify. The author is continuing his researches on this substance.

Methylene Sulphate, or Sulphuric Methylal.—Marcel Delépine.—Under the name of methylene sulphate or sulphuric methylal, the author proposes to designate a neutral crystalline product, $\text{CH}_2\text{<O>SO}_2$ or $\text{CH}_2\text{O} \cdot \text{SO}_3$, which he obtained by the union of equal molecular proportions of formic aldehyde and sulphuric anhydride. By reason of its neutrality, it is considered as neutral sulphuric ether of hypothetical methylenic glycol, $\text{CH}_2\text{<OH>OH}$, of which are known the simple ethers CH_2Cl_2 , CH_2Br_2 , CH_2I_2 , diacetic ether ($\text{CH}_2(\text{O} \cdot \text{CO} \cdot \text{CH}_3)_2$), oxalic ether ($\text{CH}_2\text{<O>C}_2\text{O}_2$), &c. The author describes the preparation, properties, and principal reactions of this substance.

A Method of Synthesising Parabanic Acid.—P. Cazeneuve.—Parabanic acid has been synthesised by the interaction of urea and ethyl oxalate contained in absolute alcohol in the presence of sodium ethylate. This method of formation has been contested. The author therefore proposes to produce it by reacting with oxamide and phenyl carbonate, according to the following equation:—



Analysis showed the substance prepared by this method to have the composition C=31.40, H=1.82, N=24.62; the theoretical percentage being C=31.58, H=1.75, N=24.56. It is therefore evident that the synthesis of parabanic acid has been performed.

MISCELLANEOUS

Royal Institution.—The following are the Lecture Arrangements at the Royal Institution, before Easter:—

Mr. C. Vernon Boys, Six Christmas Lectures (specially adapted for young people) on "Fluids in Motion and at Rest." Experimentally illustrated.

Professor E. Ray Lankester, Twelve Lectures on the "Structure and Classification of Fishes."

Dr. W. H. R. Rivers, Three Lectures on "The Senses of Primitive Man."

Professor H. H. Turner, Three Lectures on "Modern Astronomy."

Dr. Charles Waldstein, Three Lectures on "Recent Excavations at Argive Heræum (in Greece)."

Sir Hubert H. H. Parry, Three Lectures on "Neglected By-ways in Music."

Mr. W. L. Courtney, Three Lectures on "The Idea of Tragedy in Ancient and Modern Drama."

The Right Hon. Lord Rayleigh, Six Lectures on "Polarised Light."

The Friday Evening Meetings will begin on January 19th, when a Discourse will be given by The Right Hon. Lord Rayleigh on "Flight." Succeeding Discourses will probably be given by the Hon. C. A. Parsons, Professor J. Reynolds Green, Mr. H. Warrington Smyth, Professor J. H. Poynting, Major Ronald Ross, Professor Frank Clowes, Sir Benjamin Stone, M.P., Professor J. Arthur Thomson, Sir A. Noble, Professor Dewar, and other gentlemen.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Volatilisation of Silica with Hydrofluoric Acid.—Will some one kindly state why H_2SO_4 is almost invariably added when silica is estimated by volatilising with hydrofluoric acid? When bodies which form volatile fluorides like alumina are present the reason is obvious enough; but why in the separation of silica and tungsten trioxide, say? A list indicating with what bodies sulphuric acid must be used, and why, would be particularly acceptable.—H. B.

MEETINGS FOR THE WEEK.

WEDNESDAY, 20th.—Society of Arts, 8. "Bi-Manual Training by Blackboard Drawing," by H. Bloomfield Bare, F.R.I.B.A.

— Microscopical, 8. "A Review of Photomicrography and its different Methods," by Edmund J. Spitta, M.R.C.S., &c.

THURSDAY, 21st.—Chemical, 8. "Condensation of Glycollic Aldehyde and Formation of α - and β -Acrose," by H. Jackson, B.A. "On Brasilin and Hæmatoxylin—Part III.," by A. W. Gilbody and W. H. Perkin, jun. "Action of Alcoholic Potash on Monobromoglutaric Ester," by N. E. Bowtell and W. H. Perkin, jun. "Mercurous Iodide" and "Interaction of Mercurous Nitrite and Ethyl Iodide," by P. C. Rây, D.Sc.

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THE CHEMICAL NEWS.

VOL. LXXX., No. 2091.

THE ANALYSIS OF TUNGSTEN COMPOUNDS.

By FRED IBBOTSON and HARRY BREARLEY.

IN some notes on the Estimation of Tungsten (CHEM. NEWS, lxxix., 64) attention is drawn by one of us to the fact that precipitated lead tungstate may be partially decomposed by a dilute acetic acid solution and yet retain the whole of the tungsten in the precipitate. Naturally one wonders whether the acetic acid could be increased until nothing but WO_3 remained undissolved, and whether, unlike acetic, some other acid could be used to leave all the WO_3 , and nothing else, undissolved.

On adding strong nitric acid, drop by drop, to a boiling solution of lead tungstate, a point is reached at which a change of colour, from white to yellow, takes place somewhat sharply. A few more c.c. of the acid and a little boiling develops the full yellow colour of WO_3 .

This process applied to the estimation of tungsten gives surprisingly accurate results. When dilute solutions of an alkaline tungstate are being dealt with, the supernatant liquid is decanted from the precipitated lead compound through a small pulp filter, the filter placed along with the precipitate, and all treated together with the nitric acid. The following results were obtained by merely filtering off the WO_3 and igniting:—

0.1320	gram.	instead of	0.1320	gram.	WO_3
0.1837	"	"	0.1848	"	"
0.0658	"	"	0.0660	"	"
0.0260	"	"	0.0264	"	"

After separating from as much as 1 gram. of iron we found:—

0.1250	instead of	0.1265
0.2160	"	0.2166
0.1665	"	0.1670
0.1610	"	0.1605
0.0800	"	0.0820
0.0280	"	0.0290

An examination of the filtrates from these precipitations showed always that an amount of WO_3 equal to 2 or 3 m.grms. was not precipitated. The accuracy of the process therefore depends on small compensatory errors.

If ammonium salts are present, the yellow colour is not developed by adding nitric acid to the precipitated lead salt; they should therefore be eliminated with caustic alkali.

A precipitate which is accurately represented by the formula PbWO_4 is obtained by adding lead acetate to a faintly ammoniacal solution of a tungstate containing also large quantities of ammonium nitrate (CHEM. NEWS, loc. cit.), but in many cases the process is not to be recommended and is frequently impossible. The ignited, more or less acid tungstate of lead precipitated from faintly acetic acid solutions may, however, be completely dissolved in warm concentrated hydrochloric acid, and the WO_3 completely precipitated therefrom by diluting with water.

It was desirable to know the degree of interference of various elements in the estimation of tungsten according to this latter method of treatment, and by what modifications of it, if any, the presence of interfering elements could be tolerated.

The following test analyses show what effect was exercised by the presence of (I.) 1 decigram. and (II.) 2 decigrams. of the element named. The figures are grms. of

tungsten recovered, the amount added in each case being 0.1454 gram.

	I.	II.
Ammonium	Should be present as nitrates.	
Sodium	Chlorides or acetates yield	
Potassium	low results.	
Barium	0.1459	0.1459
Strontium	0.1457	—
Calcium	0.1459	0.1454
Magnesium	0.1449	0.1461
Zinc	0.1462	0.1452
Cadmium	0.4454	0.1450
Manganese	0.1448	0.1459
Nickel	0.1471	0.1455
Cobalt	0.1452	0.1460
Mercury	0.1447	0.1446
Arsenic	0.1451	0.1451
Uranium	0.1456	—
Iron	0.1467	0.1447
Silicon	Interference not avoided.	
Tin		

Ba, Sr, Ca, Mg, Zn, Cd, Mn, Ni, and Co do not interfere in the least, and the WO_3 is generally quite free from any trace of them. Generally, except when the salts of the element have a characteristic colour, no indication of the presence of a foreign body is anywhere afforded.

Arsenic.—A few grms. of ammonium nitrate are added before precipitating the tungsten; any lead arsenite precipitated is disregarded, as it passes into the filtrate after treatment with HCl.

Mercury forms a precipitate with tungstates; this may also be disregarded.

Uranium forms insoluble tungstates. These cannot be disregarded, because after ignition they are not decomposed by HCl. They are soluble in a small excess of sodium carbonate, but are re-precipitated and not redissolved by a moderate excess of acetic acid. But if an excess be added *quickly*, with vigorous shaking, the solution remains clear even when boiled. The interference of uranium salts is therefore avoided as follows:—The clear solution of W and U, containing a *small* excess of soda carbonate, is heated to boiling, and 6 to 7 c.c. acetic acid, along with an excess of lead acetate, is heated simultaneously. At near the boiling-point the former solution is poured into the latter in a thin stream, with vigorous shaking. The mixed solution is just boiled, precipitate washed by decantation, &c. The WO_3 finally obtained is free from uranium.

Iron.—It is not possible to precipitate the lead tungstate and leave the iron in solution. If the iron is but partially precipitated, it is difficult to make sure that the same is not true of the tungsten also. The following process is limited by the difficulty of manipulating bulky precipitates of ferric hydrate:—

Make the mixture just alkaline, and then just acid with acetic. At this stage the tungsten is largely in combination with the iron: the portion in solution is precipitated by the addition of the lead acetate. The bulky precipitate is best washed so thoroughly by decantation that the filter is used only as a means of collecting it together. After ignition it is treated with hydrochloric acid, as though it were pure lead tungstate. Small amounts of aluminium can be similarly dealt with; chromium, however, cannot, because the ignited chromic oxide is insoluble in hydrochloric acid. As the steel-making alloys of tungsten and molybdenum are being separately dealt with, a more extended treatment of the separation of tungsten from iron, aluminium, and chromium is reserved.

Tin.—An accurate precipitation of tungsten cannot be made in the presence of tin or silicon. Tin forms compounds with tungsten which after ignition are hard, grey in colour, and not attacked by boiling hydrochloric acid. Metallic tungsten powders are said to occasionally contain tin; the usual method of treatment depends on the reduc-

tion of the stannic oxide to metal on fusing the mixed oxides with potassium cyanide.

Silicon.—Bernouilli (CHEM. NEWS, v., 116) attacks insoluble tungstates by fusion with sodium carbonate. After neutralising the aqueous extract with acetic acid, he says, "The silica, if there be any, is completely separated by a slight excess of acetic acid, and may be separated by filtration." Surely some important item is missing from this description. Silica cannot be completely precipitated from the solution of an alkaline tungstate by the use of acetic acid. If it is not eliminated somehow, the tungsten cannot be precipitated completely with lead acetate. In spite of large excesses of this reagent, the presence of silicates causes part of the tungsten to pass into solution. Sometimes the filtrate is clear, sometimes opalescent; in either case it is generally possible to form a further precipitate on re-boiling. The deficiency seems to be due to the formation of silico-tungsten compounds which are not completely precipitated by lead salts. On the other hand, mercurous silico-tungstate being a very insoluble body, the whole of the tungsten may be precipitated with mercurous nitrate from a neutral solution, the silica in the ignited residue being removed by hydrofluoric acid. Mercurous nitrate seems generally to be available for the precipitation of tungsten where there is a probability of the formation of complex tungsten compounds, e.g., antimonio-tungstates (Hallopeau, *Journ. Chem. Soc.*, Abs., ii., 1898, 540). Formerly silica and tungstic oxide were most frequently separated by ammonium hydrate or carbonate; material has been prepared for more than one atomic weight determination even, on the assumption that a reliable separation could be so made. Dufty, in a paper read before the Sheffield Metallurgical Society (summarised in Arnold's "Steel Works Analysis"), showed that the separation was imperfect because silica was soluble in ammonia. This observation was confirmed by Benneville, in whose previous work (*Journ. Iron and Steel Inst.*, 1895, i., 205) the separation by means of ammonia had been employed. The persistent way in which this analytical error has been perpetuated shows how comparatively rarely analytical processes are verified before adoption, and how an erroneous process may live on, or even be originated and accepted, in spite of previously published evidence invalidating it. This particular error lay in the assumption that silica was insoluble in ammonia at least after, if not before, ignition; and, so long ago as 1868, Skey (CHEMICAL NEWS, vol. xvii., p. 165) showed that both before and after ignition silica was soluble in ammonia, whilst Pibram (CHEMICAL NEWS, vol. xvii., 227) determined its solubility when variously treated.

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THE RAPID EVALUATION OF METALLIC TUNGSTEN POWDERS.*

By FRED IBBOTSON and HARRY BREARLEY.

SUCH metallic tungsten powders as are used in steel-making contain over 90 per cent of tungsten, up to 4 per cent silica, about the same amount of iron, up to a few tenths per cent each of sulphur and manganese, frequently a little molybdenum, occasionally some niobium and tin, up to 3 per cent carbon, and a very variable amount of sodium tungstate and oxygen, so that an exhaustive analysis of this material is a lengthy affair.

The most important constituent is, of course, tungsten. To describe a rapid process for the estimation of this element is the chief object of this note. The estimation of the other elements is less frequently made, and there seems to be no established procedure respecting them.

The usual process for estimating the tungsten in these

powders is:—Oxidise to WO_3 by heating to redness, drive off SiO_2 with HF, fuse with sodium carbonate, precipitate from neutralised solution with HgNO_3 , and ignite to WO_3 . It is usual to operate on half a grm. The only objections to be raised to this process are:—The final WO_3 is frequently contaminated with a little SiO_2 ; the small amount of material used makes small errors very serious; and the time absorbed from first to last is considerably greater than is desirable.

We cannot claim for the following process the theoretical accuracy of the one just outlined; we are, however, assured by experience that it gives as near an approximation to the truth as can be obtained by the longer process when applied to the comparatively pure material used in steel making; at the same time it provides other interesting and useful information.

The process is:—Weigh out 3 grms. into a counterpoised platinum dish, ignite to WO_3 , and weigh (A); treat with HF and re-weigh (B). The difference = SiO_2 . Add water and pure NaHO about half the size of a walnut; boil finally after diluting to 200–300 c.c., and filter through paper pulp; keep filtrate and washings (a); Ignite residue and weigh (C); dissolve in small amount of HCl (which it should do completely if properly roasted at the beginning); dilute to several times the volume, filter, ignite, and weigh the precipitated WO_3 (D); preserve the filtrate (b); then—

$B = \text{WO}_3 + \text{Fe and Mn compounds of } \text{WO}_3$.

The Fe and Mn in these latter compounds are represented by C–D.

$\therefore B - C + D = \text{amount of } \text{WO}_3 \text{ from 3 grms. of the original powder.}$

The calculation—and also the usual amount of WO_3 which the iron, manganese, &c., carry along with them—may be illustrated by an actual example:—

Weighed dish	22.9400	(1)
After adding 3 grms. powder		
and igniting	26.5710	(2)
After HF	26.4823	(3)

$(2) - (3) = 0.0887 = 3 \text{ per cent } \text{SiO}_2$.

Insoluble in NaHO	0.0703	
WO_3 from HCl solution	0.0400	
	0.0303	(4)

(3)	26.4823
(1)	22.9400
	3.5423
(4)	0.0303

$3.5120 \text{ } \text{WO}_3 = 92.84 \text{ per cent W.}$

Some results obtained in the foregoing manner are here compared with the mean of two or more estimations made by precipitating with HgNO_3 , &c.:—

Percentage W.		Other analytical items.			
Rapid process.	Precipitation with HgNO_3 .	C.	Si.	Fe.	S.
93.70	93.86	0.87	0.51	—	—
97.70	97.54	0.05	—	—	—
96.10	96.10	0.02	—	—	—
92.80	92.94	2.46	1.40	1.00	—
95.10	95.09	1.15	0.84	0.28	—
94.50	94.49	3.41	0.24	0.42	—
93.30	93.32	0.81	0.76	0.84	—
94.90	94.81	1.54	0.51	—	—
95.00	94.90	0.65	0.52	0.53	1.28
95.50	95.20	0.43	0.93	0.38	0.22

The filtrate (a) and the residue (D) contain the whole of the tungsten, so that a direct estimation may be made if desired. The filtrate (b) contains the manganese and iron, which are separated and estimated in the usual way. The iron is not always present in the metallic state.

In our experience only sulphur has been found to affect the results. Sometimes the sulphur is almost completely evolved as H_2S on treating with dilute HCl , or as SO_2 on roasting in the muffle; in such cases it does not interfere. Sometimes, however, the sulphur is not evolved on roasting, and then the rapid process gives results too high. But as metallic tungsten loaded with sulphur, however it may exist, is not used in steel making, this source of error only rarely crops up, and is then open to very easy detection.

Although tungsten powders are not completely decomposed by aqua regia, the sulphur compounds appear to be. It is, however, nearly as expeditious to fuse with powdered potassium nitrate over a spirit-lamp, pour the dissolved melt into boiling HCl , evaporate nearly to dryness, and precipitate a fraction of the filtrate with barium chloride, &c.

Oxygen is an important constituent. Owing to the high atomic weight of tungsten, the presence of only 2 per cent of oxygen is equivalent to nearly 10 per cent of tungstic trioxide. Lower oxides of tungsten, too, are frequently indicated by the colour given to the dilute HCl when looking for sulphur. A determination of the oxygen by difference is unsatisfactory, as are all such determinations. A direct determination of the WO_3 is more or less accurately made by gently heating with a large volume of strong hydrochloric acid. It has been asserted that this has not the slightest action on the metallic tungsten, and it completely dissolves WO_3 which has not been heated. We propose to go fully into this point shortly.

Carbon may be accurately estimated by simple heating in a current of oxygen, and, if a capacious platinum boat be used, the residue may be employed for the estimation of Si, W, Fe, and Mn, as just described. Glistening spangles of what appear to be sublimed MoO_3 are frequently seen after the boat is drawn from the heated tube; these, when invisible to the naked eye, are detected on examining the broken up residue with a lens.

Ferro-tungsten may be, but it is not safe to assume that all alloys of tungsten which oxidise to a soft powder are, decarbonised by simple ignition. An alloy containing 20 per cent nickel, which yielded a soft orange pulverulent powder, was only decarbonised to the extent of 70 per cent. There is no difficulty, however, in any case in making combustions with PbO_2 or Pb_3O_4 in the same manner as for ferro-chromiums (CHEMICAL NEWS, vol. lxxv., p. 241).

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ON FLUORINE IN MINERAL WATERS. FLUORISED WATERS.

By CHARLES LEPIERRE.

IN a recent article, M. Parmentier (*Comptes Rendus*, May 1, 1899), after having shown that the corrosion sometimes observed on glass placed in contact with certain mineral waters is due simply to an adherent deposit of silica, and not, as some people believe, to fluorine or its compounds, terminates his paper with the following words: "It has also been thought that the waters of Mont-Dore, as well as other waters, contain fluoride of calcium in solution. We have never, in the numerous analyses of mineral waters we have made, been able to detect the slightest trace of any fluorine compound whatever."

One may therefore conclude that in the mineral waters examined by M. Parmentier fluorides were not present,* or that their existence was most exceptional. To my mind this statement is much too far-reaching, and I hope

* Since then (*C. R.*, June 5, 1899) M. Parmentier has remarked that he was only referring to the waters Mont-Dore and of Sainte-Honoré-les-Bains. The ambiguity, however, of the above-quoted sentence nevertheless exists.

I may be permitted to express my opinion on this subject, an opinion also based upon the results of a number of analyses of mineral waters.

Without here recalling the classic work of Nicklès, Gouvenain, Sainte Claire Deville, &c., on the presence of fluorides in water, I may remark that the greater number of modern chemists who have dealt with this subject have often found fluorine. M. Willin, whose authority is unquestioned in France, found it in the waters of Plombières, Bourbonne-les-Bains, &c. The same thing occurred in Germany (Fresenius, Bunsen, &c.). In Portugal the chemists who have dealt with the analysis of mineral waters have often found fluorides (Ferreira da Silva, Sousa Reis, and myself) in waters from Moledo, Cucos, Entre os Rios, Luso, &c. But, as a rule, the fluorides exist only as traces, and are nearly always imponderable. There are, however, certain waters, though rare, which are rich in fluorides; the most interesting example, perhaps unique in Europe, that I know of is that of the mineral water from Gerez in the north of Portugal.

These waters are much frequented, and have a truly remarkable effect in the case of maladies of the liver (from simple congestion to cirrhosis); they, however, contain only a very small proportion of mineral matter. Sousa Reis, who made the first complete analysis of this water, gives the total residue as 0.296 grm., and Le Pierre puts it at 0.310 grm. Each litre contains 22 to 25 m.grms. of an alkaline fluoride, probably that of sodium; this corresponds to 10 or 12 m.grms. of combined fluorine. Such quantities cannot be overlooked, as they represent about one-tenth of the total residue. It is sufficient to evaporate down half a litre of Gerez water in a platinum crucible to show in the most positive manner the existence of fluorides in the residue.

The analytical detection of fluorine in water may be done in four manners: 1, by the classic method (corrosion of lines drawn on glass covered with wax) by heating the residue with sulphuric acid, and closely following the instructions given by Fresenius and Nicklès; 2, if there is an excess of silica present SiF_4 can be formed, and its decomposition in the presence of water forms a very sensitive reaction; 3, by the methods of Lannes and Carnot; 4, I have often had recourse to the formation of crystals of fluosilicate of sodium, of which the small hexagonal pyramidal prisms are very characteristic (the microchemical reaction of Boricky); this last reaction is very sensitive.—*Bull. Soc. Chim.*, Series 3, vol. xxi., No. 18.

ON THE CONCENTRATION OF SULPHURIC ACID IN IRON VESSELS.

By E. HARTMANN.

ON account of the great rise in the price of platinum, the question of the concentration of sulphuric acid in vessels made of some other metal than platinum must be faced. Platinum is still employed on a very large scale, but the form of apparatus used has been greatly modified; the vessels used are much lighter than formerly, and are therefore cheaper. For some time past the author has been successfully using apparatus made of cast-iron, and we here gives some details which are certainly justified by the importance of the subject.

Acid at 54–55° B is placed in lead receivers in which it is concentrated to 61° B. It here attains a temperature of 145 to 150° C., and at this point it is run into a small cast-iron dish; it there reaches a temperature of about 180°, and a strength of 63.5–64° B. It is then run into the two actual concentrating vessels made of cast-iron, and arranged in the form of cascade. The acid from this apparatus has a strength of from 97 to 98 per cent of monohydrated sulphuric acid. The small evaporator weighs about 1200 kilos.; the two concentrators, with the domes, tubes, &c., have a weight of about 7500 kilos., so

that the whole represents a weight of about 8700 kilos. These figures apply to the apparatus giving 5500 to 6000 kilos. of acid per diem with a strength of 66° B., or 97—98 per cent of monohydrated acid. The distillate from the two principal vessels is passed, by means of two cast-iron tubes, to the refrigerators. The acid from the first has a strength of 35° B., that of the second being 60—62° B.; the latter is both clear and pure. It is again passed through the first apparatus, and acid of 66° B. strength is produced, which, though not altogether limpid, is still clear and transparent.

The small evaporator lasts about three or four months; this is certainly not a very long time, but as I shall show later on, this drawback cannot be compared with the low cost when we consider the small weight, only about 1200 kilos. The first concentrator should last six or nine months, the second a year, and even longer.

It is, of course, understood that the cast-iron must be of special quality. It should be hard, and as free as possible from all impurities. The disposition of the apparatus should also, in the author's opinion, be such that all parts should be in contact with the fire.

We should therefore require, allowing twelve months for the second concentrator:—

	Marks.
3750 kilos. of cast-iron for the first evaporator	
at 0.25 mark	= 937.50
7500 kilos. for the first concentrator	= 1835.00
4800 kilos. for the preliminary concentration	= 1200.00
Total	4012.50

During this time the apparatus will have given about 20,000 tons of monohydrated sulphuric at 97—98 per cent, so that one ton of acid at 66° B. requires a capital outlay in cast-iron of two marks, or say 0.20 mark per 100 kilos. We may add that the value of the old iron is not here taken into consideration.

According to Lunge, and the author's own personal experience, the loss of platinum is from 12.9 pfennigs per 100 kilos. of acid at 1.8, that is to say, commercial acid at 92—93 per cent; that is from 1 to 1.5 grms. per ton of acid at 98 per cent, which represents an actual cost of 1980 marks per kilo.; this represents an actual nett loss of 19.8 to 29.7 pfennigs. These figures show that, as far as cost goes, the use of cast-iron for the construction of apparatus for the concentration of sulphuric acid does not surpass that incurred by the use of platinum, but it is evident that the initial outlay for cast-iron is altogether negligible when compared with the cost of platinum apparatus. A complete installation capable of yielding 6000 kilos. of acid at 97—98 per cent would cost no less than 15,000 marks, while the production of an equal quantity of acid in platinum vessels necessitates the use of two Delplace boilers, which, with the refrigerators and condensers, amounts to about 50 kilos. of pure platinum, or close on 10,000 marks.

From the above it can be seen that the use of cast-iron apparatus merits serious attention on the part of manufacturers of sulphuric acid, unless they wish to produce an acid absolutely free from iron. On the other hand I would remark that the iron dissolved is readily deposited in acid at 66° B., traces only remaining in solution. Thus a sample of acid at 66° contained 95.4 per cent of H_2SO_4 , and only 0.015 per cent of Fe_2O_3 ; another sample from the same source contained 97.1 per cent of H_2SO_4 and 0.010 per cent of Fe_2O_3 .—*Chemiker Zeitung*, 1899, p. 147.

Christmas Lectures at the Royal Institution.—On Thursday afternoon next (December 28th) Mr. C. Vernon Boys, F.R.S., will deliver the first of a Course of Six Christmas Lectures, specially adapted for young people, at the Royal Institution. The subject will be "Fluids in Motion and at Rest" (experimentally illustrated). The remaining Lectures will be on December 30, and January 2, 4, 6, 9, 1900.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING NOVEMBER 30TH, 1899.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To the Water Examiner, Metropolis Water Act, 1871.

London, December 11th, 1899.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 208 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Nov. 1st to Nov. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 208 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during November was 2.52 inches, the whole of which fell in eight days before the 11th. The thirty years' average for this month is 2.42 inches; we thus get an excess of 0.1 inch, being the first excess since April; the total deficiency for the year is now reduced to 3.74 inches, or 15.8 per cent.

Our bacteriological examinations of 496 samples have given the results recorded in the following table; we have also examined 35 other samples, from special wells, stand-pipes, &c., making a total of 531 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	355
New River, filtered (mean of 121 samples) ..	13
Thames, unfiltered (mean of 26 samples) ..	3724
Thames-derived waters, from the clear water wells of eight Thames-derived samples (mean of 267 samples)	11
Ditto ditto highest	140
Ditto ditto lowest	0
River Lea, unfiltered (mean of 25 samples) ..	513
River Lea, from the East London Company's clear water well (mean of 32 samples) . .	7

Considering the season of the year, the London water supply continues to be of exceptional purity; and what is more remarkable is that all the water companies have been able to supply water of equally good bacteriological quality. During the month of November no less than 531 samples of the London supply have been bacteriologically examined, and the results show that the Thames-derived water was substantially of identical quality with that obtained from the River Lea and the New River, although the initial microbic impurities of the unfiltered Thames water were greatly in excess of those of either of the other sources. This is a proof of the highly efficient character of the general filtration as at present in operation.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

THE OCCLUSION OF HYDROGEN BY METALLIC COBALT AND OTHER METALS.*

By GREGORY PAUL BAXTER.

IN the course of the work upon the atomic weight of cobalt, described in preceding papers from this laboratory (Richards and Baxter, *Proc. Amer. Acad.*, 1897, xxxiii., 115; 1899, xxxiv., 351; 1899, xxxv., 61), it became necessary to weigh metallic cobalt, which had been reduced from the bromide and from the oxide by means of hydrogen. A few experiments were made at the time to show that the metal in question did not occlude appreciable amounts of hydrogen, but the comparison of this result, with the conflicting accounts of others, showed that the subject was worthy of further attention.

Hempel and Thiele (*Zeit. Anorg. Chem.*, xi., 93), by quantitative combustion of metal reduced from the oxide at a high temperature, obtained no water. Neumann and Streintz (*Monatsh. Chem.*, xii., 642), on the other hand, also working with material obtained from the oxide, found that their cobalt occluded in one case 150 times, in another 50 times, its volume of hydrogen. Troost and Hautefeuille (*Comptes Rendus*, lxxx., 788) determined the occluded hydrogen by heating the metal in a vacuum and measuring the gas evolved. Ingots of cobalt, after ignition in hydrogen, yielded only 0.1 their volume of occluded gas; foil obtained by electrolysis evolved 35 volumes of hydrogen, and upon heating in hydrogen was found to have taken up 24 volumes, while powdery cobalt, obtained by reduction of the oxide, evolved 100 times its volume of hydrogen. This latter preparation proved to be pyrophoric in air, even after the hydrogen had been removed. Neumann and Streintz also observed the same property in their cobalt when exposed to an atmosphere of oxygen.

Although this evidence seems contradictory at first sight, in reality much can be said on both sides. Metallic cobalt shows widely different characteristics in its behaviour toward hydrogen according to its purity and the method by which it is prepared. In some cases the present work shows it to have occluded only traces of hydrogen or none at all; in others it occluded amounts comparable with those found by Neumann and Streintz, and Troost and Hautefeuille.

In the following experiments the occluded hydrogen was determined by the method already mentioned—combustion of the metal and determination of the water formed. For this purpose the following apparatus was used:—

Three columns of beads moistened with strong sulphuric acid were followed by a tube containing phosphoric anhydride. These were connected with a combustion tube, which contained the boat with the metal under examination, and beyond the boat a coil of copper oxide. This copper oxide was prepared by igniting a roll of copper gauze in oxygen. Beyond this apparatus was a weighed phosphoric pentoxide tube, and this in turn was connected with an aspirator through an unweighed safety drying tube.

Owing to the fact that the organic matter emanating from rubber upon combustion will yield water, rubber was wholly avoided in this apparatus, with the exception of the connections necessary for making attachment to the combustion tube. All other joints were made wholly of glass.

After the introduction of the boat containing the cobalt into the combustion tube, and before the absorption bulb was attached, a slow current of air was drawn through the tube for some time, while the copper oxide was heated to dull redness. The weighed bulb was then inserted in the

circuit, and the section of the tube containing the boat was heated until oxidation of the metal took place. In order to avoid removal of oxygen from the air, which should finally fill the absorption bulb, the current of air was continued until the boat had become cool.

After each analysis the phosphoric anhydride bulb, which could be closed by means of glass stop-cocks, was wiped with a damp cloth, and allowed to stand in the balance-case one-half hour. Needless to say, before the bulb was weighed the pressure inside and out was equalised by opening one of the stop-cocks. As the time between two successive weighings was never more than two hours, and usually not more than one, atmospheric conditions did not change sufficiently to necessitate weighing the bulb by substitution, so this precaution was omitted.

Several blank experiments were carried out in which the average gain in weight of the bulb per hour was 0.2 gm. In another case a tube, the volume of which was 13.0 c.c., filled with pure hydrogen at the room temperature, was inserted in the apparatus, and the water formed by the combustion of the hydrogen was collected in the bulb. The weight of the water formed in two experiments was 0.0111 gm. and 0.0107 gm., while theory required 0.0108 gm. Evidently the apparatus was effective for its purpose.

In several instances, which have already been described (*Proc. Amer. Acad.*, xxxiv., 355), pure cobalt reduced from the bromide was heated to 500° in a hard glass tube, from which the air had previously been completely exhausted by a Sprengel air-pump. In no case was a measurable quantity of gas evolved, and the cobalt did not lose in weight. Although at the time the evidence seemed sufficient to show that this cobalt did not possess the property of occluding important amounts of hydrogen when heated in this gas, a few grms. of metal reduced from the bromide were subjected to quantitative combustion. In calculating the volumes of occluded hydrogen, given under the following analyses, the specific gravity of cobalt is assumed to be 8.5, and the weight of a litre of hydrogen, at 20° and 760 m.m. pressure, to be 0.0839 gm.

I. 2.5 grms. of cobalt yielded 0.0005 gm. of water, or 2.0 volumes of hydrogen.

II. 2.5 grms. of cobalt yielded 0.0010 gm. of water, or 4.0 volumes of hydrogen.

III. 2.5 grms. of cobalt yielded 0.0004 gm. of water, or 1.6 volumes of hydrogen.

In analyses II. and III. the original cobalt was reduced and reoxidised, and it can be seen that this treatment produced no appreciable effect upon the amount of the occluded hydrogen. It was evident that cobalt reduced from the bromide does not possess the property of occluding hydrogen to an important extent.

On the other hand, cobalt reduced originally from the oxide was found to contain amounts of hydrogen varying widely with the purity and the method of preparation. Cobalt oxide, free from alkalis and silica, was obtained by dissolving electrolytic metal in the purest nitric acid, and precipitating the cobalt as hydroxide by the addition of pure re-distilled ammonia, all in platinum vessels. No attempt was made to remove other impurities, since these could not have been present in sufficient quantities to produce an appreciable effect. This oxide was reduced in hydrogen at 400°—500°, and the metal was subjected to combustion as soon as cold. The weight of cobalt given is somewhat higher than it should be, owing to the fact that it is impossible to obtain complete reduction at the temperature employed. It will be shown later that a temperature sufficiently high to produce complete reduction alters the behaviour of the metal toward hydrogen.

IV. 2.0 grms. of cobalt yielded 0.0034 gm. of water, or 19 volumes of hydrogen.

V. 6.4 grms. of cobalt yielded 0.0105 gm. of water, or 19 volumes of hydrogen.

VI. 2.9 grms. of cobalt yielded 0.0053 gm. of water, or 21 volumes of hydrogen.

* Contributions from the Chemical Laboratory of Harvard College. From the *American Chemical Journal*, Vol. xxii., No. 5, Nov., 1899. (The investigation on the atomic weight of cobalt, of which this paper formed a part, was presented to the Faculty of Arts and Sciences of Harvard University as a thesis for the degree of Ph.D. in 1899).

As has already been suggested by Richards and Cushman (*Proc. Amer. Acad.*, xxxiv., 333), the cause of this great difference in behaviour might be explained by either of two hypotheses. The sodic bromide contained in the cobaltous bromide might be the agent which prevented the occlusion in the case of metal reduced from the bromide, or the volatility of the cobaltous bromide might allow the reduced metal to be deposited in a form essentially different from that reduced from the oxide. Two simple experiments served to decide this dilemma. In the first place the same 2.5 grms. of cobalt reduced from the bromide were leached with pure water until all soluble matter had been removed. After drying and heating in hydrogen the metal was again subjected to combustion.

VII. 2.5 grms. of cobalt yielded 0.0004 gm. of water, or 1.6 volumes of hydrogen.

The first conception that the sodic bromide protected the reduced metal was evidently at fault. Furthermore, cobalt oxide that had been precipitated in the presence of much sodic chloride by means of sodic hydrate, and which consequently contained a large amount of alkaline and siliceous impurity, was reduced as usual with the intention of determining the effect of this alkali. Upon removing the boat containing the metal from the reduction tube spontaneous oxidation took place, and it was found necessary to replace the hydrogen in the reduction tube, after it was cool, by nitrogen, and to insert the tube bodily between the drying train and the combustion tube. This cobalt differed from the samples previously examined in that it did not contract or "sinter" to any extent. Whether this effect was due to the alkalis or to silica is uncertain.* One determination of the hydrogen occluded by metal treated in this way was made.

VIII. 2.0 grms. of cobalt yielded 0.0085 gm. of water, or 48 volumes of hydrogen.

Evidently the impurities did not protect the cobalt from the hydrogen; hence one is driven to accept the second solution of the dilemma, and to decide that cobalt reduced from the bromide differs in its state from that obtained from the oxide.

The experiment already described of heating in a vacuum cobalt reduced from the bromide was now repeated with metal obtained from the oxide. In every case gas was evolved during this process, as would have been expected, and the metal upon combustion proved to contain only traces of hydrogen.

IX. 2.7 grms. of cobalt yielded 0.0008 gm. of water, or 3.5 volumes of hydrogen.

X. 5.0 grms. of cobalt yielded 0.0010 gm. of water, or 2.5 volumes of hydrogen.

XI. 5.0 grms. of cobalt yielded 0.0014 gm. of water, or 3.2 volumes of hydrogen.

That no appreciable amount of hydrogen was given off at ordinary temperatures was evident from the following analyses. The cobalt was placed in a hard glass tube, which was then exhausted, while cold, with a Sprengel air-pump. After this treatment it was subjected to combustion as usual (Analyses XII. and XIII.), and the oxide remaining from the combustion was again reduced, and the metal analysed for hydrogen as soon as cold (Analyses XIV. and XV.). It can be seen that the amounts of hydrogen obtained in the two cases are essentially the same.

XII. 2.5 grms. of cobalt yielded 0.0017 gm. of water, or 7.6 volumes of hydrogen.

XIII. 2.7 grms. of cobalt yielded 0.0035 gm. of water, or 14.8 volumes of hydrogen.

XIV. 2.5 grms. of cobalt yielded 0.0019 gm. of water, or 8.6 volumes of hydrogen.

XV. 2.7 grms. of cobalt yielded 0.0029 gm. of water, or 12.3 volumes of hydrogen.

This was further shown by passing dry air first over

cold freshly reduced metallic cobalt, and then over hot copper oxide. The small amount of water formed was collected in the usual way, and is entirely in agreement with the preceding results.

XVI. 2.0 grms. of cobalt yielded 0.0006 gm. of water in one hundred and fifty minutes.

Troost and Hautefeuille, however, found that cobalt which contained one hundred times its volume of hydrogen gave up a considerable part of it in a vacuum without the application of heat.

In several analyses in which cobalt was allowed to stand in hydrogen for at least twenty-four hours at the room temperature, the amount of water obtained upon combustion was considerably larger than that obtained from metal which was subjected to combustion immediately after reduction.

XVII. 2.7 grms. of cobalt yielded 0.0160 gm. of water, or 68 volumes of hydrogen.

XVIII. 2.9 grms. of cobalt yielded 0.0117 gm. of water, or 46 volumes of hydrogen.

The metal of Analysis XVIII., when analysed immediately after reduction, yielded 0.0053 gm. of water.

In order to show that this difference was not due to a change in the metal itself (owing to the process of oxidation and reduction), equal amounts of the same preparation of oxide were reduced under conditions exactly similar. One sample (Analysis XIX.) was allowed to stand in hydrogen at the room temperature for twenty-four hours; the other sample (Analysis XX.) was subjected to combustion as soon as cold.

XIX. 2.3 grms. of cobalt yielded 0.0043 gm. of water, or 21 volumes of hydrogen.

XX. 2.3 grms. of cobalt yielded 0.0022 gm. of water, or 11 volumes of hydrogen.

From this fact that long-continued standing in cold hydrogen increases the amount of gas occluded, it is evident that cobalt possesses the property of taking up hydrogen at ordinary temperatures. This occlusion progresses only slowly in the cold, however, for the amount taken up in twenty-four hours was less than that occluded during ordinary reduction and cooling. In the following cases the metal was first heated in a vacuum, and then allowed to stand in an atmosphere of hydrogen for twenty-four hours at the room temperature.

XXI. 2.7 grms. of cobalt yielded 0.0020 gm. of water, or 8.5 volumes of hydrogen.

XXII. 2.7 grms. of cobalt yielded 0.0018 gm. of water, or 7.5 volumes of hydrogen.

The same metal, after reduction and cooling in hydrogen, yielded 0.0035 gm. of water.

Cobalt reduced in hydrogen and allowed to cool in pure nitrogen occluded only traces of hydrogen.

XXIII. 1.9 grms. of cobalt yielded 0.0004 gm. of water, or 2.1 volumes of hydrogen.

XXIV. 1.9 grms. of cobalt yielded 0.0010 gm. of water, or 5.4 volumes of hydrogen.

This same cobalt, when cooled in hydrogen, yielded 0.0029 gm. of water upon combustion, or nearly 16 volumes of hydrogen.

According to Neumann and Streintz, repeated oxidation and reduction of the metal diminish its power of occluding hydrogen. From one sample they obtained first 150 volumes of hydrogen, then 50 volumes. Johnson, working with copper, noticed the same peculiarity, which is exhibited to a less striking extent by the metal used in the following two series of analyses:—

XXV. 2.7 grms. of cobalt yielded 0.0035 gm. of water, or 14.8 volumes of hydrogen.

XXVI. 2.7 grms. of cobalt yielded 0.0029 gm. of water, or 12.3 volumes of hydrogen.

XXVII. 2.7 grms. of cobalt yielded 0.0025 gm. of water, or 10.5 volumes of hydrogen.

XXVIII. 2.7 grms. of cobalt yielded 0.0035 gm. of water, or 14.8 volumes of hydrogen.

XXIX. 2.7 grms. of cobalt yielded 0.0025 gm. of water, or 10.5 volumes of hydrogen.

* Richards and Cushman found that nickel which had been "purified" in glass vessels contained enough of these two impurities to prevent its sintering when reduced in hydrogen (*Proc. Amer. Acad.*, xxxiv., 328).

XXX. 2.7 grms. of cobalt yielded 0.0018 gm. of water, or 7.5 volumes of hydrogen.

XXXI. 2.2 grms. of cobalt yielded 0.0020 gm. of water, or 10.2 volumes of hydrogen.

XXXII. 2.2 grms. of cobalt yielded 0.0012 gm. of water, or 6.2 volumes of hydrogen.

XXXIII. 2.2 grms. of cobalt yielded 0.0019 gm. of water, or 9.9 volumes of hydrogen.

XXXIV. 2.2 grms. of cobalt yielded 0.0012 gm. of water, or 6.2 volumes of hydrogen.

During the above process the metal gradually sintered together, occupying apparently much less volume than at first. If the same metal is then heated to redness in hydrogen it sinters much more still, and yields only traces of hydrogen.

XXXV. 5.5 grms. of cobalt yielded 0.0016 gm. of water, or 3.5 volumes of hydrogen.

XXXVI. 6.2 grms. of cobalt yielded 0.0004 gm. of water, or 0.7 volume of hydrogen.

XXXVII. 2.5 grms. of cobalt yielded 0.0003 gm. of water, or 1.2 volumes of hydrogen.

Even impure oxide, obtained by igniting commercial nitrate, when heated to a high temperature in hydrogen, occluded only traces of this gas.

XXXVIII. 1.8 grms. of cobalt yielded 0.0004 gm. of water, or 2.5 volumes of hydrogen.

Metal reduced from impure oxide at low temperatures is not coherent but powdery, while pure metal shows a decided tendency to cling together. Pure metal reduced at high temperatures forms a hard solid mass. This sintering can be nothing more nor less than incipient fusion (compare Richards, *Am. Chem. Journ.*, 1898, xx., 725). Where the minute particles of metal are in close contact with one another the contraction takes place very readily, while impurities keep apart the particles of metal and necessitate the application of higher temperatures to produce the same effect.

From the results of the work just described several important conclusions can be drawn. Cobalt in the form of ingots, which present a minimum amount of surface, is known to occlude almost no hydrogen. On the other hand, cobalt reduced from the oxide at a low temperature, and consequently in a very finely divided condition, offers a maximum amount of surface, and occludes relatively large amounts of hydrogen. Electrolytic foil, which, although it possesses considerable porosity, still lies between the above two modifications in relative surface, falls between them also in the amount of hydrogen retained. Neither Neumann and Streintz, nor Troost and Hautefeuille, took any precautions to purify their cobalt from alkalis or silica. Their metal, kept from sintering together by the impurities and the low reduction temperature, was in the finest state of division; consequently it proved to be pyrophoric, and to occlude maximum amounts of hydrogen, just as in Analysis VIII. of this paper. That this property of spontaneous oxidation was not due to the hydrogen, but to the large amount of surface presented to the air, is shown by the fact that the metal used by Troost and Hautefeuille was still pyrophoric after it had been heated in a vacuum. The pure metal used in the work just described sintered considerably, even at the lowest temperature at which reduction took place, and accordingly occluded much less hydrogen than the impure metal; while even approximately pure metal, when heated to a high temperature, sintered together to such an extent that a minimum surface was presented to the hydrogen, and only traces of this gas were occluded.

The first inference is perfectly clear. The volume of occluded hydrogen depends upon the amount of surface presented, which, in the case of metals reduced from the oxide, varies with the purity of the metal and the temperature of reduction.

Again, since at ordinary temperatures the occlusion of hydrogen progresses very slowly (Analyses XXII. and XXIII.), while at the temperature of reduction, 400°–500°, it amounted to an almost negligible quantity

(Analyses XXIV. and XXXV.), at some intermediate temperature the occlusion must progress at a maximum rate.

Thirdly, the time during which the metal is in contact with the hydrogen is an important factor in determining the quantity of this gas taken up.

Finally, the volatility of cobaltous bromide evidently allows the metal reduced from it to be deposited in a form more compact and coherent than that reduced from the oxide, since the presence of sodic bromide was found to have no perceptible effect upon the amount of occluded gas.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 7th, 1899.

Professor THORPE, F.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Alexander Hutcheon Bennett, 61, London Road, Bromley, Kent; Oscar Joseph Cole, Wivenhoe, Colchester, Essex; Thomas Cuthbert Davison, 49, Victoria Road, New Swindon, Wilts.; Harry Medforth Dawson, Yorkshire College, Leeds; Stephen M. Dixon, University, Fredericton, New Brunswick, Canada; James Foulds, 5, Murray Street, Burnley, Lancashire; Robert W. Gray, 7, Orme Court, Bayswater; Henry Jackson, Downing College, Cambridge; Thomas Goode Joyce, The Smallthorns, Stafford; William Charles Robert Kynaston, 9, Harland Road, Higher Tranmere, Birkenhead; Arthur Robert Laws, 48, Waverley Terrace, Newcastle-on-Tyne; Alan W. Cranbrook Menzies, 11, Howe Street, Edinburgh; Edgar Ford Morris, 69, Shrewsbury Street, Old Trafford, Manchester; Herbert Newall Morris, 48, Lansdowne Road, Crumpsall, Manchester; Ernest Brooks Naylor, 73, Castle Street, Bolton; James Hart-Smith, 4, Edenvale Street, Fulham; Bertram Vincent Storr, 17, York Road, Ilford, Essex; Archie Hugh Strong, Stoneleigh Villa, 63, Herne Hill Road, Camberwell, S.E.; Gustavus Athol Waterhouse, "Ellerslie," Birrell St., Waverley, N.S.W.; Leonard Philip Wilson, 123, Chadwick Road, East Dulwich, S.E.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Messrs. James William Anderson; Francis Paul Armitage; Frederick William Armstrong; Frederic Arnold Beesley, B.Sc.; Edgar Marsh Chapman; John Arthur Dewhurst; James Dick Dougall; Frank Rawlinson Dudderidge; H. F. F. Burdett Fermor; Elliott Henry Gurney; Percy Kay, Ph.D.; Henry Wulff Kinnersley; Ernest F. Stephen Lange; William Thomas Leeming, B.Sc.; Stephen Joshua Lett; Edward Watkin Lewis; William D. McCreath; Hugh Main, B.Sc.; Harry Ainley Neale; Thomas Henry Palmer; Marchant Pearson, B.A.; Bennett C. Polkinghorne, B.Sc.; Georges Ponthieu; Frank J. Pye; William Downing Raynor, B.A.; Christopher Foulis Roundell, B.A.; William Russell; Robert Hawks Walton; F. R. Leyland Wilson, M.A.; John Wilson.

Of the following papers, those marked * were read:—

*151. "*The Oxidation of certain Organic Acids in presence of Ferrous Salts.*" By HENRY J. HORSTMAN FENTON, M.A., F.R.S., and H. O. JONES, B.A., B.Sc.

The oxidation of various organic substances in presence of iron has formed the subject of a considerable number of previous communications, and the observations are now being extended in several directions. The present paper deals with results which have recently been obtained in an extensive study of the behaviour of acids of typical

constitution when oxidised by hydrogen peroxide in presence of ferrous salts.

It is shown that, under the conditions of the experiments, the following acids are unacted upon by the reagent:—Acetic, monochloracetic, oxalic, malonic, succinic, dibromosuccinic, fumaric, maleic; whereas an energetic, and generally immediate, oxidation occurs in the case of the following acids:—Formic, glycollic, lactic, β -oxybutyric, glyceric, tartronic, tartaric, malic, citric, mucic, saccharic, pyruvic, dioxytartaric, acetylene dicarboxylic, acetone dicarboxylic, pyromucic, benzoic, picric.

The oxidation products obtained are often of considerable interest, and changes can be effected which have not been accomplished by any other means. These oxidation products are being examined, and in the present communication an account is given of the progress of the investigation.

*152. "*Oxalacetic Acid.*" By HENRY J. HORSTMAN FENTON, M.A., F.R.S., and H. O. JONES, B.A., B.Sc.

By the oxidation of malic acid in presence of ferrous salts, the authors obtained a white crystalline substance having the formula $C_4H_4O_5$, which, on examination, was found to be free oxalacetic acid. The hydrazone crystallises in lustrous prisms, and, when heated with dilute sulphuric acid, gives the phenylpyrazoloncarboxylic acid which was obtained by Wislicenus and by Buchner from the ethyl and methyl esters. Further identification is afforded by the formation of the methyl ester and its hydrazone, by the colour reaction with ferric chloride, and by the formation of pyruvic acid when an aqueous solution of the acid is heated.

*153. "*Determination of the Constitution of Fatty Acids. Part II.*" By ARTHUR WILLIAM CROSSLEY and HENRY RONDEL LE SUEUR.

In continuation of their work (*Trans.*, 1899, lxxv., 161) the authors have prepared ethylisopropylacetic acid from ethylisopropylmalonic acid, and have investigated it by their method.

Ethylisopropylmalonic acid crystallises from benzene in glistening needles melting at $131-131.5^\circ$; the *ethyl* salt is a colourless liquid boiling at $232-233^\circ$.

Ethylisopropylacetic acid, $C_2H_5 \cdot CH(C_3H_7) \cdot COOH$, prepared by the elimination of carbon dioxide from ethylisopropyl malonic acid, is a disagreeable smelling liquid boiling at 203° . The *ethyl* salt is a colourless liquid boiling at $164-165^\circ$ (765 m.m.), and possessing a characteristic smell; the *amide* crystallises from light petroleum in silky needles melting at 134° ; the *anilide* separates from light petroleum in clusters of small glistening needles melting at $114-115^\circ$; and the *paratoluidide* forms feathery needles melting at 123° .

Ethyl α -bromethylisopropylacetate is a mobile liquid boiling at $135-136^\circ$ (59 m.m.), possessing a pungent smell somewhat resembling peppermint. When treated with diethylaniline, hydrogen bromide is eliminated in two ways, giving rise to a liquid having a marked odour of peppermint, and boiling at $175-180^\circ$. It consists of a mixture of *ethyl dimethylethylacrylate* and *ethyl methylisopropylacrylate*. On saponification, a mixture of the corresponding acid is obtained boiling constantly at 136° (55 m.m.).

When this mixture is oxidised, first with potassium permanganate, and then potassium dichromate, the products are, as expected, acetone, acetic, propionic, and isobutyric acids; thus proving that two unsaturated ethyl salts are formed by the action of diethylaniline on ethyl α -bromethylisopropylacetate.

Applying these results to the determination of the constitution of the original acid, having the formula $C_7H_{14}O_2$, since acetone is produced on oxidation, the group $(CH_3)_2C:$ must be attached to the α -carbon atom in the unsaturated acid, the double bond being produced by elimination of a bromine atom from the α -carbon atom, and a hydrogen atom from an adjacent carbon atom, hence $(CH_3)_2C:C \cdot COOH$ represents the grouping of five of the

seven carbon atoms. The two remaining carbon atoms must be attached to the α -carbon atom, and, as propionic acid was obtained, they must have been present as an ethyl group, therefore the formula of the unsaturated acid is $(CH_3)_2C:C(C_2H_5) \cdot CO_2H$. and $(CH_3)_2CH \cdot CH(C_2H_5) \cdot CO_2H$ that of the original fatty acid.

The presence of acetic and isobutyric acids is accounted for by the oxidation of the second unsaturated acid produced, namely, methylisopropylacrylic acid.

*154. "*The Reaction between Sulphuric Acid and Potassium Ferrocyanide.*" By R. H. ADIE, M.A., B.Sc., and K. C. BROWNING, B.A.

The authors have made a quantitative investigation of the action of sulphuric acid of concentrations varying from that of H_2SO_4 (98 per cent) to $H_2SO_4, 8H_2O$ on potassium ferrocyanide with the following results:—

The salt dissolves in acid of strengths corresponding to H_2SO_4 and H_2SO_4, H_2O , with the formation of potassium sulphate and hydroferrocyanic acid; there is only a slow and incomplete formation of carbon monoxide.

In acid of the strength represented by $H_2SO_4, 2H_2O$, the decomposition of the salt results in the formation of carbon monoxide: this reaction accounts for all the cyanogen in the salt.

With more dilute acid of the composition of from $H_2SO_4, 4H_2O$ to $H_2SO_4, 10H_2O$, the products are hydrocyanic acid and Everitt's salt, $K_2Fe_2Cy_6$. At the latter dilution all the cyanogen in the salt appears as hydrocyanic acid, while the formation of carbon monoxide practically ceases with acid of $H_2SO_4, 4H_2O$ strength.

The authors discuss the mechanism of the reaction (i.) through the formation and hydrolysis of hydroferrocyanic acid by means of the dilute sulphuric acid; (ii.) through the action of the potassium sulphate first formed on the hydroferrocyanic acid, with the intermediate formation of Everitt's salt. The latter reaction only takes place in fairly concentrated solutions, whilst the former alone occurs with acids more dilute than that represented by $H_2SO_4, 10H_2O$. Other conditions influencing the reactions are also fully discussed.

*155. "*The Sulphates of Bismuth.*" By R. H. ADIE, M.A., B.Sc.

The author has investigated the conditions of formation and limits of existence of the sulphates of bismuth, and has found that from sulphuric acid of any strength between those represented by $H_2SO_4, 6H_2O$ and $H_2SO_4, 12H_2O$, a basic bismuth sulphate having the formula $5Bi_2O_3, 11SO_3, 17H_2O$ crystallises out; if between $H_2SO_4, 3H_2O$ and $H_2SO_4, 5H_2O$, the sulphate may be represented as $Bi_2O_3, 4SO_3, 7H_2O$, and if the strength be between H_2SO_4, H_2O and $H_2SO_4, 2H_2O$, the salt obtained has the composition $Bi_2O_3, 4SO_3, 3H_2O$. From sulphuric acid itself, the sulphate which crystallises out at temperatures above 170° has the formula $Bi_2O_3, 4SO_3, H_2O$; if below 170° , $Bi_2O_3, 4SO_3, 10H_2O$.

This temperature 170° is that at which the acid sulphates are decomposed when heated in an air-bath, the normal bismuth sulphate, $Bi_2O_3, 3SO_3$, being formed.

156. "*On Sulphates of the Form $R_2SO_4, 2MSO_4$, especially those of Isometric Crystallisation.*" By F. R. MALLETT.

During an examination of langbeinite, $(K_2SO_4, 2MgSO_4)$, from the Punjab (*Min. Mag.*, 1899, xii., 159), the author noticed that the mineral, which fuses at a red heat, on cooling solidifies to a more or less distinctly crystalline mass. This observation naturally suggested that the salt might probably be artificially produced by fusing potassium and magnesium sulphates together in the proper proportions. The crystalline mass obtained on cooling the fused sulphates contains especially in the cavities abundant octahedral crystals sometimes over a millimetre in diameter.

As it seemed probable that other salts of similar constitution might be produced in the same way, the author has prepared the following sulphates of isometric sym-

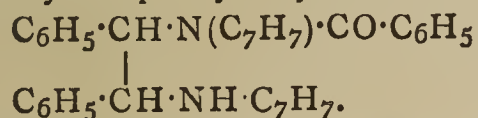
metry: $K_2SO_4, 2MgSO_4$; $K_2SO_4, 2ZnSO_4$; $K_2SO_4, 2MnSO_4$; $K_2SO_4, 2NiSO_4$; $K_2SO_4, 2CoSO_4$; $Rb_2SO_4, 2MgSO_4$.

Measurements of the angles of the crystals, and partial or complete analyses of the above salts, are given: their mode of decomposition by absorption of water is also described.

Mixed crystals of isometric symmetry containing more than two of the above metals have also been produced, as well as various anisotropic salts, which have not as yet been examined in detail.

157. "Reactions of the so-called Dibenzylamarine." By FRANCIS R. JAPP, F.R.S., and JAMES MOIR, M.A., B.Sc.

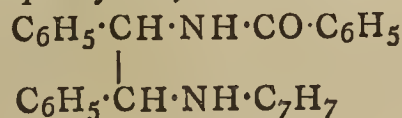
In a recently published note (*Proc.*, 1899, xv., 211), the authors showed that the compound melting at $139-140^\circ$, obtained by Claus and Elbs (*Ber.*, 1880, xiii., 1420) by the action of potassium hydroxide on dibenzylamaronium chloride, and described as dibenzylamarine, is in reality benzoyl-*s*-dibenzyl-*i*-diphenylethylenediamine—



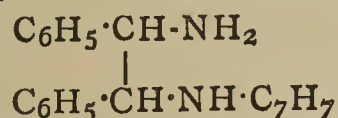
The following are various experimental results obtained in the study of this substance.

Action of Nitrous Acid.—This yields, as chief product, a nitroso-compound, $C_{21}H_{17}(C_7H_7)_2N_2(NO)O$ (dimorphous: short needles, m. p. 166° ; and oblong laminæ, (m. p. 168°), together with dibenzylamaronium nitrate, $C_{21}H_{17}(C_7H_7)_2N_2 \cdot NO_3$, and a little lophine. The second of these three compounds was also prepared from dibenzyl amaronium chloride and silver nitrate, thus proving its constitution. When "dibenzylamarine" nitrate, $C_{21}H_{18}(C_7H_7)_2N_2O, HNO_3$, was heated at 185° , it was converted into a mixture of dibenzylamaronium nitrate and the foregoing nitroso-compound. Dibenzylamaronium nitrite (from the quaternary chloride and silver nitrite) is an uncrystallisable gum, quite distinct from the isomeric nitroso-compound.

Reduction with Hydriodic Acid.—By boiling "dibenzylamarine" with hydriodic acid (sp. gr. 1.7) for some hours, the following products were obtained:—As chief product, benzoylbenzyl-*i*-diphenylethylenediamine,—



(minute needles, m. p. 218° , basic, and yielding a nitroso-compound (m. p. 246°); benzyl-*i*-diphenylethylenediamine,—



(slender needles, m. p. 90° , converted by benzoic chloride into the foregoing compound melting at 218°); and, further, dibenzyl, benzylic iodide, benzoic acid, benzylamine, and ammonia.

Action of Sodium in Boiling Alcohol.—An almost quantitative yield of Grossmann's *s*-dibenzyl-*i*-diphenylethylenediamine (*Ber.*, 1889, xxii., 2301) was obtained.

Action of Potassium Hydroxide.—No action takes place in alcoholic solution at 150° , but on fusing the compound with potassium hydroxide it yielded the foregoing *s*-dibenzyl-*i*-diphenylethylenediamine, together with benzyllophine, and a crystalline non-basic substance melting at 128° , which gave figures agreeing with the formula $C_{28}H_{24}N_2O$.

Oxidation.—The authors confirmed Claus's observation that "dibenzylamarine" is not altered by boiling with chromium trioxide in glacial acetic acid solution, but found that when a little concentrated hydrochloric acid was added to the mixture, oxidation took place on boiling, and benzoylbenzyl-*i*-diphenylethylenediamine, $C_{28}H_{26}N_2O$ (m. p. 218°)—already obtained in the reduction with hydriodic acid—was formed.

Action of Heat.—The chief products were lophine and benzyllophine.

158. "Note on Isoamarine." By H. LLOYD SNAPE, D.Sc., Ph.D.

As Japp and Moir have recently published (*Proc.*, 1899, xv., 211) their reasons for regarding the isomeride of amarine described by Brooke and the author (*Trans.*, 1899, lxxv., 208) as a racemic form of amarine, the author wishes to report that he has succeeded in separating this isomeride, by means of tartaric acid, into two varieties of equal and opposite optical activity. The author hopes to give a detailed account of these and other experiments on isoamarine at an early date.

159. "On the Preparation of Benzene Azo-orthonitrophenol." By J. T. HEWITT, M.A., D.Sc.

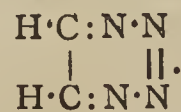
Noelting (*Ber.*, 1887, xx., 2997) has observed that the nitration of benzeneazophenol in a strong sulphuric acid solution leads to the formation of paranitrobenzene azophenol, $NO_2 \cdot C_6H_4 \cdot N:N \cdot C_6H_4 \cdot OH$. The author of the present communication finds that by nitrating benzeneazophenol (10 grms.) with dilute nitric acid [20 c.c. nitric acid (sp. gr. 1.36) and 60 c.c. water] at 40° , the product of the reaction is benzene-azo-orthonitrophenol, $C_6H_5 \cdot N:N \cdot C_6H_3(NO_2)(OH)$, m. p. 128.5° (corr.). This difference in behaviour can be readily explained, since Noelting nitrated a sulphate of benzeneazophenol, which is probably a derivative of quinone phenylhydrazone, $C_6H_5 \cdot NH \cdot N:C_6H_4:O$, whilst the author of the present paper chose nitric acid of such a dilution as to exclude salt formation, and hence nitrated benzeneazophenol, $C_6H_5 \cdot N:N \cdot C_6H_4 \cdot OH$, itself. The result is not compatible with Hantzsch's formulation of the azophenols as quinone-hydrazones when in the free state (*Ber.*, 1899, xxxii., 3089), since, while phenols are more readily substituted than benzene nuclei not containing hydroxyl or amino-groups, on the other hand amino-derivatives of benzene are certainly more easily substituted than quinones. Certain derivatives of benzene-azo-orthonitrophenol are described in the paper.

160. "Some New Osazones and Tetrazones." By HAROLD A. AUDEN.

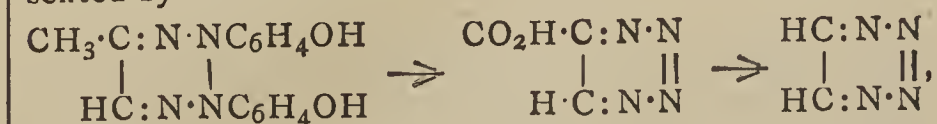
None of the three possible isomeric forms of tetrazine (which may be described, according to the relative positions of the ring components, as *v*-, *s*-, or *a*-tetrazines) has yet been isolated. Derivatives of the first of these are represented in the osotetrazones obtained by Pechmann by the oxidation of osazones (*Ber.*, 1888, xxi., 2751). A benzene derivative has also been obtained by Hempel (*J. Pr. Chem.*, xli., 176), and perhaps the substances named diazohydrides by Zincke (*Ber.*, 1886, xix., 1451; 1888, xxi., 543) belong to this class.

Representatives of *s*-tetrazine have been obtained by Ruhemann (*Trans.*, 1888, liii., 850; 1889, lv., 242; 1890, lvii., 50) and Pinner (*Ber.*, 1893, xxvi., 2126; 1894, xxvii., 984, 3273). Ruhemann (*Trans.*, 1899, lxxv., 1131) has obtained a dihydro-derivative of *s*-tetrazine ("tetrazoline") from monoformylhydrazine, and Pellizzari (*Atti R. Acad. Lincei*, [5], 1899, viii., 327) from diformylhydrazine.

The author has prepared certain osazones and tetrazones with a view to obtaining from them, by a process of oxidation, *v*-tetrazine,—



The various stages of the oxidation may probably be represented by the formulæ—

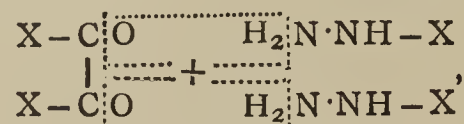


similar to those in the cases of osotriazole (*Annalen*, 1891, cclxii., 303), tetrazole (*Ber.*, 1895, xxviii., 1688), and triazole (*Ber.*, 1885, xviii., 1550, 2907).

The methods which may be used for the preparation of the substances dealt with in the paper are as follows:—

1. The action of nitrosoacetone on hydrazines, with the intermediate formation of hydrazoximes. 2. The inter-

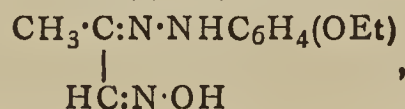
action of diketones and hydrazines. In the former case, it is not necessary to isolate the nitrosoacetone, but by so doing the reaction is more under control and the yield consequently increased by 1 to 2 per cent. In the latter method, the reaction may be thus represented by—



yielding the osazone which, by careful oxidation by means of dilute acetic acid and potassium dichromate or by amyl nitrite, loses two atoms of hydrogen, forming the corresponding tetrazone. The latter method gave better yields, the hydrazoximes frequently decomposing with the production of uninviting resinous products. In attempting to oxidise the tetrazones, further difficulties have been met with, due partly to their great stability, and partly to the difficulty in some cases of producing the tetrazone from the osazone. The actions of various oxidising agents have been studied, especially those of potassium permanganate in alkaline solution at 80–100°, and of amyl nitrite. It may here be pointed out that oxidation in acid solution is excluded because of the tendency of tetrazones to form triazole derivatives, as shown by Pechmann. A mixed osazone was also prepared, as it seemed probable that this might yield a "tetrazolium" on oxidation similar to the product obtained by Pechmann and Wedekind (*Ber.*, 1894, xxvii., 320), and that this in turn might yield further interesting products.

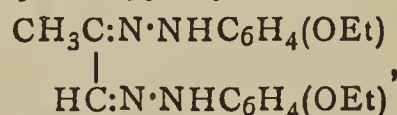
Although the experiments as yet carried out have not led to the isolation of *v*-tetrazine, the following substances have been prepared:—

Methylglyoxal-p-ethoxyphenylhydrazoxime,—



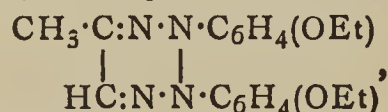
brownish yellow plates, with golden-yellow reflex, melting at 104–106°, with rapid decomposition. It can be re-crystallised from methyl alcohol, but in solution is unstable.

Methylglyoxal-p-ethoxyphenylosazone,—



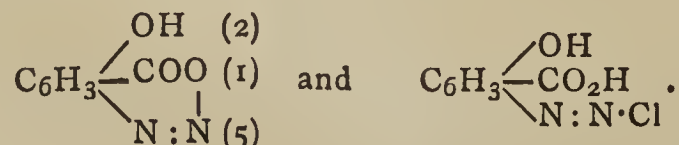
reddish yellow needles, m. p. 135. With strong sulphuric acid it gives deep green solution.

Methylglyoxal-p-ethoxyphenylosotetrazone,—



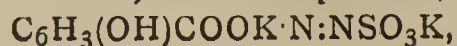
crystallises in Bordeaux-red needles, which cannot be distinguished in shade from those of methylglyoxalosotetrazone. It dissolves in strong hydrochloric acid with indigo-blue colouration, which disappears on heating; with strong sulphuric acid it gives a similar colouration, rapidly becoming green. It is not attacked by alkaline potassium permanganate in the cold, and only with difficulty at 100°.

Diazosalicylic acid,—



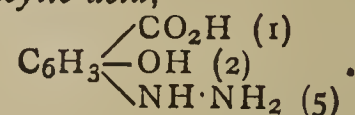
The former explodes at 155°, the latter about the same temperature, decomposition generally beginning about 10° lower. The chloride loses hydrogen chloride in the desiccator over soda and when exposed to the air. The free diazo-compound varies in shade from yellow to greenish yellow; the chloride forms nearly colourless needles. If only gently heated, both may be re-crystallised from water.

Potassium diazosalicylic acid sulphonate,—



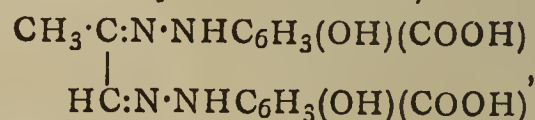
is a fairly stable compound which may be re-crystallised from water, and dried at 100°. It crystallises in yellow plates.

Hydrazine salicylic acid,—



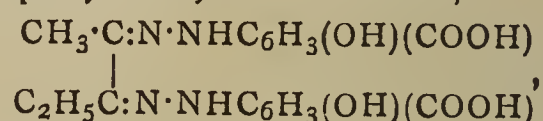
This is a slightly brown amorphous powder which melts at 148°. The hydrochloride crystallises in snowy needles which char at 150°. It reduces Fehling's solution slowly in the cold, and gives a white crystalline hydrazone with benzaldehyde.

Methylglyoxal salicylic acid osazone,—



a bright yellow crystalline powder, m. p. 192°. It gives a dark green colouration with ferric chloride. The corresponding hydrazoxime could not be isolated, and probably does not exist, as on using only one molecule of hydrazine the osazone was formed.

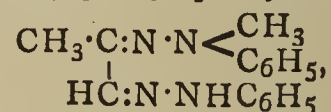
Acetyl propionyl salicylic acid osazone,—



may be obtained in very small yellow crystals by adding water to its solution in alcohol.

On boiling the crude product with alcohol, a yellow residue was invariably left; this residue melted at 220°, but yielded the same numbers on analysis as the more soluble portion which melted at 197°, and is possibly a stereoisomeride. This substance is apparently attacked by oxidising agents, but it does not give the osazone reaction. It yielded, on oxidation with potassium permanganate or potassium ferricyanide, small amounts of a white crystalline substance which gave a characteristic wine-red colouration with ferric chloride.

Methylglyoxal-methylphenylphenylosazone,—



yellow needles (m. p. 119–120°), slightly darker in shade than methylglyoxalphenylosazone, gives a deep red colouration with strong sulphuric acid.

The author is led to publish this preliminary note now, as, owing to a loss through fire of notes and products, some months must elapse before the results of the oxidation experiments can be published in detail.

161. "A Series of Substituted Nitrogen Chlorides. Part II. The Trichloro-phenyl-acyl-nitrogen Chlorides." By F. D. CHATTAWAY and K. J. P. ORTON.

This paper is a continuation and completion of the authors' previous work on the substituted nitrogen chlorides which are directly obtainable from formanilide, acetanilide, and benzanilide.

It is shown that in anilides the formation of a nitrogen chloride or bromide in all cases precedes substitution in the nucleus, and that the degree of difficulty with which the transformation of these nitrogen chlorides and bromides can be effected corresponds with the relative difficulty of obtaining the transformation products directly by the action of the halogen.

The following compounds are described:—

2 : 4 : 6 - Trichloro-phenyl-formyl nitrogen chloride, $\text{C}_6\text{H}_2\text{Cl}_3\cdot\text{NCl}\cdot\text{CHO}$, brilliant white prisms terminated by domes, m. p. 78°; 2 : 4 : 6 - trichloro-phenyl-acetyl nitrogen chloride, $\text{C}_6\text{H}_2\text{Cl}_3\cdot\text{NCl}\cdot\text{COCH}_3$, white transparent prismatic crystals resembling cubes, m. p. 74°; 2 : 4 : 6 - trichloro-phenyl-benzoyl nitrogen chloride, $\text{C}_6\text{H}_2\text{Cl}_3\cdot\text{NCl}\cdot\text{COC}_6\text{H}_5$, thick white prisms terminated by pyramids, m. p. 89°; p-chloro-phenyl-benzoyl nitrogen chloride, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NCl}\cdot\text{COC}_6\text{H}_5$, glistening short white prisms with domed ends, m. p. 79.5°.

These compounds all show the general reactions characteristic of the nitrogen halogen linkage.

162. "The Reaction between Cupric Sulphate Solution and Magnesium, Zinc, and Iron." By R. M. CAVEN, B.Sc., F.I.C.

When magnesium, zinc, or iron reacts with cupric sulphate solution, the usual assumption of simple replacement of metal by metal is in no case found to be exactly true; cuprous oxide invariably occurs to a greater or less extent together with metallic copper in the residue.

The suggestion of Divers (*Proc.*, 1898, xiv., 57) that the cuprous oxide formed in the reaction with magnesium is due to the production of cuprous sulphate, is well in accord with the facts established; but the separation of cuprous oxide is not connected with the formation of the basic cupric sulphate produced by hydrolysis, as suggested by Divers, since it is produced in considerable quantity, together with an equivalent amount of sulphuric acid, in hot strong solutions, in which spontaneous hydrolysis of cupric sulphate with separation of insoluble basic salt does not occur. That the cuprous oxide is produced by the hydrolysis of cuprous sulphate is borne out by all the facts; and this view is supported by the observations of F. Foerster (*Zeit. Elektrochemie*, 1897, iii., 479, 493).

In all the reactions examined, with the exception of that of iron reacting with cold solutions, hydrogen is evolved, though sometimes in small quantity only. J. B. Senderens states that hydrogen is evolved in this case also (*Bull. Soc. Chim.*, 1897, [3], xvii., 271), though his statement is not confirmed by the experiments of the author.

In those cases in which only copper and cuprous oxide appeared in the residue, the hydrogen evolved was calculated from the deficiency of the acid remaining in the solution from the quantity equivalent to the cuprous oxide found. This agreed with actual measurement; and also the sum of the equivalents of the copper, cuprous oxide, and hydrogen, thus calculated, was equal to the quantity of the displacing metal employed.

The evolution of hydrogen in each case is due to one or more of the following distinct causes:—

I. Reaction of displacing metal with sulphuric acid produced—

- a. By hydrolysis of cupric sulphate, resulting in separation of insoluble basic cupric salt (Divers).
- b. By hydrolysis of cuprous sulphate, resulting in separation of cuprous oxide.

II. Action of the metallic couple upon the water of the solution.

III. Very slight reaction of finely-divided precipitated copper with hot dilute sulphuric acid, produced according to I.b.

In all cases except that of magnesium reacting with dilute solution, in which case the permanent separation of basic compounds takes place, the evolution of hydrogen may be eventually referred to the acid produced by hydrolysis of cuprous sulphate only.

The production of cuprous oxide and sulphuric acid in appreciable amount and in equivalent quantities when cupric sulphate solution is brought into contact with finely-divided copper under various conditions, shows that cuprous sulphate is produced synthetically in the above reactions. It is, however, believed that in most cases cuprous sulphate is also formed by the reduction of cupric sulphate by the replacing metal.

Camphenylone.—E. E. Blaise and G. Blanc.—The authors' experiments show that bases obtained by reducing campholenic nitrile are essentially different from dihydroaminocampholene and to the α and β aminocampholenes. Camphenylone and its derivatives do not contain the trimethylcyclopentanic radicle which exists in bodies belonging to the camphor series. The theoretical treatment of this subject appeared in a paper published in the *Bull. de la Soc. Chim. de Paris*.—*Comptes Rendus*, cxxix., No. 22.

NOTICES OF BOOKS.

The Metallurgy of Lead and Silver. By HENRY F. COLLINS, Associate of the Royal School of Mines, &c. Part I. LEAD. Being one of a series of Treatises on Metallurgy, written by Associates of the Royal School of Mines. Edited by Sir W. C. ROBERTS-AUSTEN, K.C.B., D.C.L., F.R.S. With numerous Illustrations. London: Charles Griffin and Co., Limited. 1899. Pp. 368.

THE matter contained in this volume (Part I.) deals with the whole method of lead smelting. The American and German methods having been recently so thoroughly dealt with by other authors, they are only treated in a condensed manner, supplemented by information from other sources, forming a digest of the whole in a compact form.

The book is divided into three Sections and eighteen chapters. Section I. is introductory, and deals with sampling and assaying, the chemical and physical properties of lead and lead ores; these ores are for metallurgical purposes divided into two classes, viz., "sulphide ores" consisting principally of galena mixed with varying proportions of blende, pyrites, fahlerz, &c., and "oxidised ores," called in America "carbonates," which include not only cerussite, but all its mixtures with anglesite, pyromorphite, &c.

Section II. deals with the smelting of lead ores, which is practically the only method of separating lead from its ores; wet methods have been tried from time to time, but have not proved commercially successful.

The three principal methods of treatment are: 1, the *roast and reaction* method; 2, the *roast and reduction* method; and 3, the *precipitation* method. These methods are rarely employed quite independently of each other, for the residues of the first method are almost always worked up by the second or third methods, while the second method is almost always combined with the third, and often with the first as well. This Section, which forms the major part of the book, viz., 233 pages, describes all the various furnaces, hearths, and other mechanical appliances used in lead smelting, as well as in Chapter XI. examples of smelting as practised all over the world. Chapter XII. is on flue dust, its composition, collection, and treatment, and Chapter XIV. deals with the treatment of zincic sulphides. A very useful feature for facilitating reference and comparison is that details of the practice at particular localities have been as far as possible put into the form of tables; these will be found in nearly every Chapter.

Section III. is on desilverisation, in which the Pattinson and Parkes processes are both fully described and compared. The chief advantages of the Pattinson process are that it is of less complexity and requires simpler plant, and in the case of a fairly pure lead from reverberatory or hearth smelting it readily yields a lead of specially high quality. It is, however, not well suited to the treatment of impure blast-furnace lead, rich in silver, or gold-bearing. The Parkes process, on the other hand, is from 20 to 50 per cent cheaper to work; it produces a lead containing only 4 to 6 dwts. of silver against 9 to 15 dwts. by the Pattinson process; traces of gold are completely recovered, and it produces a lead for cupellation with 2000 to 5000 ozs. of silver per ton against 500 to 650 ozs. by the Pattinson process.

The Australian method of smelting and desilverisation are described in considerable detail for the first time in this volume. The ores treated are siliceous and ferruginous carbonates containing some galena, and are smelted at the Broken Hill works in fifteen 80 ton furnaces.

The whole of this valuable work is put together in an admirable manner, and may well be described as "thorough." The author, besides being an old pupil of Sir W. C. Roberts-Austen at the Royal School of Mines, has also had the benefit of his valuable assistance in editing the work; in fact, the touch of the master hand is apparent

throughout. The book is well printed and handsomely bound, its external appearance being an index of its internal excellence:

A Handbook of Physics and Chemistry. Adapted to the requirements of the First Examination of the Conjoint Examining Board of the Royal Colleges of Physicians and Surgeons, and also for general use. By HERBERT E. CORBYN, B.Sc.(Lond.), and ARCHIBALD M. STEWART, B.Sc.(Lond.), Science Master of King Edward's Grammar School, Chelmsford. With 120 Illustrations. London: J. and A. Churchill.

THIS book is intended to aid students in the preparation for the first examination in physics and chemistry of the Royal Colleges of Physicians and Surgeons, and it is hoped that it will be useful also to those preparing for the examinations of the Pharmaceutical Society and the Royal Veterinary College. So long as the examination system remains as it is we suppose works of this kind will be necessary to aid the student to pass, but after studying the work we cannot help feeling that the man who has passed may have a very superficial knowledge of the sciences involved. We are glad to see that the author, in his preface, points out that "it will be necessary for the student to supplement his reading by practical work in the laboratory."

The explanations and analogies in the introduction to physics are original and good, but some of the matter in this section is decidedly poor! For instance, on page 30 there is a description of the now well-known Sprengel air-pump which, to say the least, is decidedly obsolete, and must date back quite twenty years. We scarcely expected this in an up-to-date book. Also on page 35 instructions are given for the manufacture of a mercurial thermometer which would sadly vex the most painstaking student. It is a pity that in the electrical section no description is given of the useful influence machine introduced by Mr. Wimshurst, while a whole page and a wood-cut is devoted to a very old form of plate glass friction machine.

The chemical section is by far the best part of the book, and is well and clearly written, and as complete as can be for the space devoted to it. In the list of elements we note that the name beryllium is used instead of glucinum, and that while helium is included no notice is taken of the decomposition of didymium into neodymium and praseodymium. In Appendix A will be found a choice selection of examination problems with their answers, and there is a good paragraph index.

An Elementary Course in Practical Physics. By F. CASTLE, M.I.M.E., Mechanical Division, Royal College of Science; Lecturer on Mechanics, Geometry, &c., Morley College, London; Author of "Notes on Advanced and Honours Theoretical Mechanics" in "The Practical Teacher." London, Edinburgh, and New York: Thomas Nelson and Sons. 1899.

THIS is a very valuable addition to that class of test-book which seeks to teach the student the accepted laws and principles of science, not by filling his mind with a mass of statistical information, but by causing him to make the experiments from which the laws and principles are deduced, using as far as possible apparatus prepared by himself.

To gain this end the author has spared no pains to bring together a considerable number of simple and ingenious pieces of apparatus, many quite original, with full instructions for their preparation.

A good example is found on page 154, in a method for showing the linear expansion of a metal bar by heat, consisting of two blocks of wood, a needle, and a straw! The advantages of the plentiful use of squared paper is pointed out, and the author seeks to impress upon the student the value of that neat and methodical method in working, without which success is impossible.

If anything, some of the instructions given seem almost

too minute, and would seem to imply a total absence of reasoning power on part of the student; the instructions for measurement of length on page 19 is an instance, but, doubtless, the author's practical experience with modern students has shown him the need for it.

Of course, in the condensation of such a volume of technical information some errors are unavoidable. We notice one in the instructions for making an alcohol thermometer on page 163, where, after having prepared and filled the tube, the student is instructed to heat it until it is full to the top of the tube and then seal! Such a procedure is necessary where mercury is used, but alcohol thermometers need to be sealed with as much air in the tube as possible.

Examinations and problems are given to be worked out, and answers are to be found at the end of the book. There is a sensible index, and a number of good illustrations.

We consider that the book will be found of real use to both students and science masters.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 22, November 27, 1899.

Action of Dry Hydrochloric Acid on Silver and the Inverse Reaction.—M. Jouniaux.—Silver is attacked by gaseous hydrochloric acid. This fact was first noticed by Boussingault, who, by passing dry hydrochloric acid over silver heated to redness, found that silver chloride was formed, hydrogen being liberated. This experiment was confirmed by M. Berthelot, who worked at 500–550°, when the dissociation of hydrochloric acid has no influence on the progress of the phenomenon. Reciprocally, silver chloride, heated in an atmosphere of hydrogen, is reduced by this gas, there being formed metallic silver and hydrochloric acid. The author studies the effect of temperature on these two inverse reactions, experiments being conducted at 350°, 440°, and 600° for the first reaction and at 490°, 530°, and 600° for the inverse reaction.

The Colouring-matter of Digitale.—MM. Adrian and A. Trillat.—The colouring-matter in question was extracted from *Digitalis luteo* by treating the residues from the preparation of crystallised digitaline. The body obtained after numerous crystallisations consists of yellow needles melting easily at a temperature of 217–218°. The author has endeavoured to find a formula for this substance by combustion and determination of the molecular weight. The mean of two experiments gives the composition—

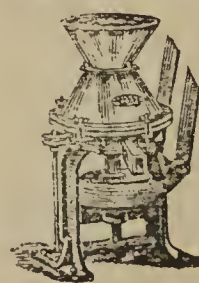
C	71.860
H	4.665
O	23.475 (by diff.)

which corresponds to a formula $(C_4H_3O)_n$, with molecular weight 253. The formula may therefore be taken to be $C_{16}H_{12}O_4$. This body is remarkable on account of its great stability and resistance of many chemical reagents.

MEETINGS FOR THE WEEK.

THURSDAY, 28th. { Royal Institution, 3. (Christmas Lectures to
SATURDAY, 30th. { Young People). "On Fluids in Motion and
at Rest," by Charles Vernon Boys, F.R.S.
(Experimentally illustrated).

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THE CHEMICAL NEWS

VOL. LXXX., No. 2092.

ON DOUBLE REFRACTION IN NAPHTHALENE AND A CHLORINATED DERIVATIVE.

By GREVILLE WILLIAMS, F.R.S.

IN the CHEMICAL NEWS for December 15th there is a notice of the Proceedings of the Physical Society, in which it is stated that Prof. S. P. Thompson read a note "On an Organic Compound of great Double Refraction." This substance is crystallised naphthalene, and it is said by Prof. S. P. Thompson to be 60 per cent more doubly refracting than Iceland spar. This most interesting announcement reminded me that many years ago in my article, "Naphthalene," in Watts' Dictionary of Chemistry, vol. iv., 1866, I called attention to the fact that tetrachloride of naphthalene crystallises from benzene in colourless transparent rhombohedrons, which, when deposited from half a gallon or a gallon of the solution, I had sometimes obtained nearly a quarter of an inch in length. I also say that they "exactly resemble calc-spar. They also possess powerfully the property of double refraction." I was not, however, aware that naphthalene itself was doubly refractive until I saw the notice of Prof. S. P. Thompson's discovery.

ON THE STABILITY OF GUN-COTTON AND SMOKELESS POWDERS.

By C. HOITSEMA.

THE author has already shown (*Moniteur Scientifique*, July, 1898, p. 500) that when gun-cotton is submitted to very slow heating, *in vacuo*, it gradually decomposes, leaving a black residue, and a gaseous product consisting at first of small quantities of the higher oxides of nitrogen, and finally of a simple mixture of nitrogen and binoxide of nitrogen. He has now observed that the unstable compounds contained in gun-cotton give rise to the higher oxides of nitrogen, while the stable gun-cotton gives only nitrogen and binoxide of nitrogen. From these observations the author has devised a new apparatus and method for determining the stability of gun-cotton.

The apparatus consists of two U-tubes, corked and connected with each other. In the first 1 or 2 grms. of gun-cotton are placed. The second contains glass-wool impregnated with Guttman's reagent (diphenylamine dissolved in sulphuric acid). The tube containing the gun-cotton is then placed in an oil-bath for a quarter of an hour, at a temperature of 110° C. At the end of this time a current of carbonic acid is passed through the apparatus for a few minutes, and the blue colouration of it is observed, indicating the presence of the higher oxides of nitrogen.

The experiment is repeated in the same manner, but each time at a temperature 10° lower than the previous one, until a point is reached when the blue colour no longer appears. This temperature is noted as the index of stability.

As can be seen, the author has endeavoured to substitute an *index of temperature* for the *index of time* which has been in use up to the present. He does not approve of the test of stability proposed by Thomas (*Moniteur Scientifique*, February, 1899, p. 145) consisting of heating gun-cotton to 94—96° until red fumes appear.

Below are given the figures found for several explosives tried by the methods of Abel (at 80°), Thomas, and Hoitsema:—

Powders.	Abel. Minutes.	Thomas. Days.	Hoitsema. ° C.
Gun-cotton (Stowmarket) ..	4	9—10	100
Do. (Walsrode) ..	33—39	10—10.5	100
Do. (Kruppamühle) ..	12	5	100
Powder (Muiden)	35	6—8	80
Do. (Cölln-Rottwell) ..	7—9	8—8.5	80
Ballistite (Muiden)	23—27	6.5—8 hrs.	70
Do. (Düneberg)	13	5.5—6 days	80
Cylindrical powder (Muiden)	48	5.5	90
Do. (Düneberg) ..	60	7—8	90

—*Zeitschrift für Angewandte Chemie*, 1899, xxx., p. 705.

THE DOUBLE AMMONIUM PHOSPHATES OF BERYLLIUM, ZINC, AND CADMIUM IN ANALYSIS.*

By MARTHA AUSTIN.

It has been shown (*Am. Journ. Sci.*, vi., 233) that the composition of the phosphate of manganese thrown down by microcosmic salt from the solution of a pure manganous salt contains more manganese than belongs to the ideal ammonium-manganese phosphate, NH_4MnPO_4 ; and, further, that by acting with ammonium chloride in proper proportion the phosphate of manganese thrown down by microcosmic salt may be completely converted to the ideal ammonium-manganese phosphate. Ammonium chloride, likewise, in the case of magnesium phosphate (*Am. Journ. Sci.*, vii., 187) tends to cause the replacement of the metal by ammonia. Indeed, the replacement here is readily carried so far beyond the point corresponding to the normal ammonium-magnesium phosphate, NH_4MgPO_4 , that the tendency to form a salt richer in ammonia and poorer in magnesium—perhaps something like $\text{Mg}(\text{NH}_4)_4(\text{PO}_4)_2$ —must be recognised.

These facts suggested an investigation into the constitution of certain other ammonium phosphates with reference to their utility in analytical processes. Of the elements of Mendeleeff's second group, beryllium, magnesium, zinc, cadmium, and mercury are capable of yielding double ammonium phosphates, while no such compounds of calcium, strontium, and barium have been described. The solubility in ammonia of the double ammonium phosphates of the elements of the former category appears to increase as the elements of which they are compounds are removed in the series from the beryllium, and, while the same is true of the simple phosphates of members of the latter category, the extent of such solvent action is slight comparatively. According to the work recorded in the literature, calcium, barium, and strontium form individually a neutral tribasic phosphate or acid phosphates of greater or less degree of acidity, according to the conditions of precipitation. In my experience, where salts of these elements were precipitated either with ammonium phosphate or microcosmic salt in presence of varying amounts of ammonium chloride or ammonia, or both, only the recognised phosphates were obtained. The effect of ammonium salts in presence of ammonia seemed to promote the formation of the tribasic salt in the case of calcium and strontium; barium tends to form the barium acid phosphate almost exclusively, even in the presence of ammonium salts and free ammonia. No doubt ammonium phosphate of either calcium, strontium, or barium was produced under any condition. As is well known, mercury does form an ammonium-mercury phosphate, but the salt is soluble to so great a degree in ammonia, am-

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. viii., September, 1899.

monium chloride, and even in the precipitant itself, that nothing of any value for analytical work seemed likely to come from its study.

The Ammonium-beryllium Phosphate.

The ammonium-beryllium phosphate has been described by Roessler (Fresenius, *Zeit. Anal. Chemie*, 1878, 148) as a crystalline salt produced by boiling some time in ammoniacal solution the phosphate precipitated by ammonium phosphate, though the best results of this treatment failed to yield the ideal constitution of this salt, NH_4BePO_4 . This same precipitate cannot be obtained, Roessler further states, by using a sodium salt as the precipitant. In order to follow out this work of Roessler, a solution of beryllium chloride for use was prepared as follows:—The pure beryllium chloride of commerce was dissolved in as little water as possible and treated for the precipitation of aluminum by ethereal hydrochloric acid (*Am. Journ. Sci.*, iv., 111). After filtering and evaporating from the filtrate the ether and a part of the hydrochloric acid, the beryllium was precipitated with ammonia, filtered to remove any members of the magnesium group, and washed free from ammonium chloride. The larger part of the precipitate was dissolved in hydrochloric acid in slight excess, and boiled with the reserved portion. After filtering, the solution was diluted to definite volume and standardised by precipitating measured portions of the solution with ammonia, filtering on asbestos under pressure in a perforated platinum crucible, igniting the residue, and weighing as the oxide. The results recorded in Section A of Table I. were obtained by precipitating definite volumes of the pure solution of beryllium chloride with ammonium phosphate in a platinum dish, dissolving the precipitate in hydrochloric acid in faint excess, and while hot precipitating slowly with dilute ammonia, boiling (while the solution was kept distinctly ammoniacal) until the flocky precipitate was entirely converted to a fine powdery, semi-crystalline, rapidly-subsiding mass. A quarter to a half hour is necessary under the most favourable conditions to cause this conversion. After cooling, the precipitate was filtered off on asbestos under pressure in a perforated platinum crucible, washed carefully with distilled water, dried, ignited, and weighed. The filtrate was tested for beryllium by boiling with ammonia. None was found in these cases, nor in any of the following work. Faint traces of chloride were found in the residues after ignition after dissolving in nitric acid and testing with silver nitrate.

The results are in every case in excess of the theory for the pyrophosphate derived by ignition of the ammonium-beryllium phosphate, possibly because the ammonium chloride present may have a tendency to form a salt too rich in ammonium (as was shown to be the case with the magnesium salt), consequently giving too much phosphoric acid in the ignited residue; or, because of inclusion of the chloride and phosphoric acid. It might reasonably be expected that some phosphoric acid may be held, since a trace of chloride was found. Either or both of these substances may have been held mechanically or in combination.

It was found that by boiling for some time the solution of beryllium chloride with microcosmic salt (6, Section B of the table), precipitating in the same manner as when ammonium phosphate was used, that the same sort of powdery mass remained as was obtained by the ammonium phosphate. The residue being tested for sodium according to the method brought out by Kreider and Breckenridge (*Am. Journ. Sci.*, ii., 263), showed sodium present to the amount of 0.0062 grm., reckoned as sodium phosphate. It may be reasonably supposed that the presence of the sodium was due to one of two causes: inclusion of the soluble phosphate, or to a tendency on the part of the beryllium to form an ammonium-sodium-beryllium phosphate (Persoz, *Liebig's Annalen*, lxxv., 174; Atterberg, *Bull. Soc. Chim.*, xxiv., 358) or a sodium-

beryllium phosphate (Scheffer, *Liebig's Annalen*, cix., 144), both of which are known to exist. Long boiling of the precipitates is tedious, and, unless great care is taken, may involve small losses of material; hence if the same results could be obtained with less boiling such treatment would be decidedly advantageous. The results in Section C of the table were obtained by adding microcosmic salt to the hot solutions of the chloride, boiling five minutes, cooling, filtering off on an ashless filter—because of the flocky condition of the precipitate—treating as usual before igniting the residue in a platinum crucible. The results compare well with those obtained by long boiling of the precipitated beryllium—although all are in excess of the theory. That ammonium chloride here, as in cases above, has a marked effect in changing the constitution of the phosphate precipitated by microcosmic salt is not readily seen. It is obvious that the presence of an excess of the soluble phosphate is essential to precipitate the beryllium as the double ammonium phosphate from the results recorded in Section D of the table, where, after the precipitate of beryllium phosphate had subsided and the supernatant liquid had been poured off, the precipitate dissolved in hydrochloric acid was brought down again at the boiling temperature with ammonia either alone or in presence of ammonium chloride. The results obtained show that the salt approaches the constitution of the tribasic phosphate, when it is precipitated in presence of a faint excess of phosphoric acid, even though ammonium chloride in large amount be present.

From the work described it is clear that the ammonium-beryllium phosphate is not obtained in ideal condition by precipitating a solution of the chloride with ammonium phosphate. Roessler's own results were likewise only approximately correct, as he states. It is also plain that hydrogen-sodium-ammonium phosphate precipitates the ammonium-beryllium phosphate in a condition as nearly ideal as does the ammonium phosphate, while the effect of the ammonium chloride in either case is not marked in producing a phosphate containing ammonia. Of most importance in obtaining the ammonium salt is an excess of the soluble phosphate, for when the amount of the precipitant is reduced to a little more than the theoretical amount the condition of the phosphate coincides almost exactly with the theory for the tribasic phosphate, even though a large excess of ammonium chloride be present. When there is an abundance of the precipitant the results are all in excess of the theory, which may be accounted for on the supposition that foreign material is included—the chloride of ammonia and the soluble phosphate—to a greater or less extent by the precipitate. The formation of a phosphate of beryllium containing too much ammonia and phosphoric acid, or, in case of the precipitations by microcosmic salt or sodium by the formation of a sodium-ammonium-beryllium phosphate and sodium-beryllium phosphate (known salts) is not definitely proved.

The Ammonium Zinc Phosphate.

Debray (*Comptes Rendus*, lix., 40), Bette (*Liebig's Annalen*, xv., 129), and Heintz (*Liebig's Annalen*, cxliii., 156) separately found that ammonium zinc phosphate is formed by boiling a solution of zinc sulphate with ammonium phosphate. This salt was investigated later by A. Guyard (Hugo Tamm, *CHEM. NEWS*, xxiv., 148), who found that if to a solution of a zinc salt of an organic or a mineral acid supersaturated with ammonia until all the zinc oxide is dissolved and made faintly acid with hydrochloric acid, sodium phosphate be added, a flocky precipitate resulted, which on being kept near the boiling point for some seconds was converted to crystalline zinc ammonium phosphate, which filtered readily, and was washed free from impurities with the greatest facility. He found that all the zinc in solution was thrown down as the ammonium zinc phosphate, which, on ignition, yielded the zinc pyrophosphate. With care in handling this process to avoid an excess of the precipitant, and the presence of sodium and potassium salts (on account of the danger of

TABLE I.

	Be ₂ P ₂ O ₇ corresponding to BeCl ₂ .			Error.	Be ₂ P ₂ O ₈ corresponding to BeCl ₂ .			Error.	(NH ₄) ₂ PO ₄ .	NH ₄ Cl.
	Taken.	Found.	Grm.		Taken.	Found.	Grm.			
	Grm.	Grm.	Grm.		Grm.	Grm.	Grm.		Grms.	Grms.
	A.				B.				HNaNH ₄ PO ₄ ·4H ₂ O.	
1.	0.3578	0.3613	0.0035 +						2	—
2.	0.3578	0.3808	0.0230 +						2	—
3.	0.3578	0.3707	0.0129 +						2	—
4.	0.3578	0.3640	0.0062 +						2	—
5.	0.3578	0.3680	0.0102 +						2	30
6.	0.3578	0.3697	0.0119 +							
	C.									
7.	0.3578	0.3618	0.0040 +						1.2	—
8.	0.3578	0.3680	0.0102 +						1.2	—
9.	0.3578	0.3729	0.0151 +						1.2	10
10.	0.3578	0.3631	0.0053 +						1.2	60
	D.									
11.					0.2700	0.2589	0.0111 —		0.5	—
12.					0.2700	0.2989	0.0289 +		0.5	—10
13.					0.2700	0.2936	0.0236 +		0.5	5—60
14.					0.2700	0.2507	0.0193 —		0.5	—60

TABLE III.

	Zn ₂ P ₂ O ₇ corresponding to ZnSO ₄ .			Error.	Error in terms of Zinc.	Zn ₂ P ₂ O ₇ corresponding to Zn left in the filtrate.	(NH ₄) ₂ PO ₄ .	NH ₄ Cl.	Time of standing.
	Taken.	Found.	Grm.						
	Grm.	Grm.	Grm.		Grm.	Grm.	Grm.	Grm.	Hours.
	A.				B.				
1.	0.6355	0.6206	0.0149 —		0.0060 —	Trace	3.13	—	1½
2.	0.6355	0.6254	0.0101 —		0.0040 —	Trace	3.13	—	16
3.	0.6355	0.6300	0.0055 —		0.0022 —	Trace	3.13	—	16
	C.				D.				
4.	0.6355	0.6271	0.0084 —		0.0034 —	Trace	4.47	0.5	1
5.	0.6355	0.6256	0.0099 —		0.0040 —	None	4.47	0.5	20
6.	0.6355	0.6285	0.0070 —		0.0028 —	None	4.47	10	½
7.	0.6355	0.6304	0.0051 —		0.0020 —	None	4.47	10	¼
8.	0.6355	0.6295	0.0060 —		0.0024 —	None	4.47	10	2½
9.	0.6355	0.6335	0.0020 —		0.0008 —	None	4.47	10	16
10.	0.6355	0.6381	0.0026 +		0.0010 +	None	4.47	20	½
11.	0.6355	0.6379	0.0024 +		0.0009 +	None	4.47	20	2
12.	0.6355	0.6386	0.0031 +		0.0012 +	None	4.47	20	½
13.	0.6355	0.6393	0.0038 +		0.0014 +	None	4.47	20	½
14.	0.6367	0.6355	0.0012 +		0.0005 +	None	4.47	30	16
	E.				F.				
15.	0.6355	0.6172	0.0183 —		0.0072 —	0.0108	0.894	20	3
16.	0.6355	I. 0.6227 II. 0.0040	0.0098 —		0.0039 —	None	I. 0.894 II. 3.576	20	½
17.	0.6355	0.6270	0.0085 —		0.0034 —	None	4.47	—	3
18.	0.6355	0.6125	0.0230 —		0.0093 —	0.0148	4.47	—	18
19.	0.6355	0.6303	0.0052 —		0.0021 —	0.0020	4.47	10	18

TABLE IV.

	Cd ₂ P ₂ O ₇ corresponding to CdCl ₂ .			Error.	Error in terms of cadmium.	Cd ₂ P ₂ O ₇ corresponding to Cd found in the filtrate.	HNaNH ₄ PO ₄ ·4H ₂ O.	NH ₄ Cl.	Time of standing.
	Taken.	Found.	Grm.						
	Grm.	Grm.	Grm.		Grm.	Grm.	Grm.	Grm.	Hours.
1.	0.6972	0.6201	0.0771 —		0.0434 —	0.0059	4.5	—	3
2.	0.6972	0.6135	0.0837 —		0.0471 —	None	4.5	—	16
3.	0.6972	0.6134	0.0838 —		0.0471 —	None	4.5	—	16
4.	0.6972	0.6792	0.0180 —		0.0101 —	Trace	4.5	1	16
5.	0.6972	0.6831	0.0141 —		0.0079 —	0.0113	4.5	10	2
6.	0.6972	0.6976	0.0004 +		0.0002 +	Trace	4.5	10	16
7.	0.6972	0.6969	0.0003 —		0.0002 —	Trace	4.5	10	18
8.	0.6972	0.6962	0.0010 —		0.0006 —	Trace	4.5	10	16
9.	0.6972	0.6891	0.0081 —		0.0045 —	0.0191	4.5	20	16
10.	0.6972	0.6972	0.0000		0.0000	Trace	4.5	20	16
11.	0.6972	0.6942	0.0030 —		0.0016 —	Trace	4.5	20	16
12.	0.6972	0.6737	0.0235 —		0.0132 —	0.0304	4.5	30	16
13.	0.6972	0.5655	0.1317 —		0.0741 —	0.1378	4.5	30	16
14.	0.6972	0.6922	0.0050 —		0.0023 —	0.0088	4.5	10	16
15.	0.6972	0.3209	0.3763 —		0.2117 —	0.2449	4.5	—	16

occlusion), the precipitation of the ammonium zinc phosphate, ignition, and weighing as the pyrophosphate made, Guyard believed, an ideal process for the estimation of zinc. Although there was slight solubility of the salt, it made an insignificant loss when the process was handled properly. Acids present, or certain alkalies to any great extent, increased the solubility of the salt so much that the loss became appreciable. Another source of error was, to Guyard's mind, loss of zinc during the ignition of the zinc ammonium phosphate with the paper on which the precipitate had been collected. Garrigues (*Fourn. Am. Chem. Soc.*, xix., 936) found, in estimating zinc in a practical way, that this process advocated by Guyard gives in solutions of zinc free from salts of all metals, even alkaline salts—solutions that from previous steps in analysis, however, must have contained ammonium chloride in large amount—as satisfactory results as Guyard claimed for it. Garrigues' method of procedure was to add acid diammonium phosphate to a warm solution of zinc exactly neutralised with either hydrochloric acid or ammonia, so that the weights of zinc ammonium phosphate and that of the diammonium phosphate added should be as one to five respectively, to heat until the flocky precipitate becomes crystalline and subsides, filtering off on asbestos, drying at 100°C ., and weighing preferably, although the residue may be ignited without loss, since the filtration is made on asbestos in a perforated crucible. Langmuir (*Fourn. Am. Chem. Soc.*, xxi., 115) modifies the method by destroying, with dilute acetic acid, any free ammonia that may be left in the solution after boiling.

In the work that follows, in which an attempt was made to show what precipitate is formed from a solution of zinc by the action of a soluble phosphate, also what effect ammonium chloride has upon the precipitate, a solution of zinc chloride prepared as detailed below was employed. The pure zinc chloride of commerce was treated with zinc carbonate, filtered and precipitated with ammonium sulphide. This precipitate was boiled in a slight excess of hydrochloric acid until all the hydrogen sulphide was removed, and then was precipitated with sodium carbonate. After washing carefully until all the chloride was removed, the greater part of the carbonate was dissolved in sulphuric acid in slight excess, boiled with the remaining portion of the carbonate, and filtered. This solution diluted to definite volume was standardised as sulphate by evaporating the solution to dryness in a platinum crucible and heating the residue (Rose-Finkener, "Analytische Chemie," 6te Auflage, vol. ii., 117). The heating is carried on safely by so placing the platinum crucible in a radiator (consisting of a crucible and a triangle), that the bottom of the platinum crucible was held about 1 c.m. above the bottom of the outside crucible. Constant weights were obtained in successive treatment with a few drops of sulphuric acid and heating over the radiator. The results obtained in this manner were a trifle higher, though in fair agreement (when the nature of the carbonate process is taken into consideration) with determinations of the zinc in the solutions as oxide after precipitating with sodium carbonate with the usual precautions, filtering off on asbestos under pressure in a perforated platinum crucible, washing with distilled water, drying and igniting. Results are given in Table II., showing the amount of zinc sulphate found in five different portions, each of 40 c.c. of the solution of zinc sulphate, and, for comparison, the results of determinations as zinc oxide by the carbonate processes are included.

TABLE II.

ZnSO ₄ found in 40 c.c.m. ³ of solution. Grm.	Mean value of ZnO corresponding to ZnSO ₄ in 40 c.c.m. ³ of solution. Grm.	ZnO found in 40 c.c.m. ³ of solution by precipitation as the carbonate. Grm.
0.5386	0.2712	0.2691
0.5385		0.2685
0.5387		0.2711
0.5387		
0.5390		

Definite portions of the solution of zinc sulphate were carefully drawn from a burette into a platinum dish, heated and treated with ammonium phosphate until the solution turned red litmus paper blue. The whole was heated until the flocky precipitate became crystalline and fell to the bottom of the dish. The solution, after standing as recorded in Section A of Table III., was filtered off on asbestos under pressure in a perforated platinum crucible, and the precipitate was washed with distilled water, dried, ignited, and weighed. The filtrate in each case, as in all following cases, was tested for zinc with sulphuretted hydrogen. The results recorded in Section B of the table were obtained in the same manner as those of Section A, with microcosmic salt substituted for the ammonium salt as the precipitant. The results are below the theory for the pyrophosphate, but no appreciable amount of zinc appeared in the filtrates. Neither ammonium phosphate nor ammonium sodium phosphate seems to precipitate the ideal ammonium zinc phosphate under these conditions, and the time of standing appears to be without effect.

The results recorded in Section C were obtained by precipitating the warm solution of the zinc in presence of large amounts of ammonium chloride by adding microcosmic salt until the solution was alkaline to litmus. From these results it seems that the presence of ammonium chloride is essential for the conversion of the zinc phosphate precipitated by hydrogen sodium ammonium phosphate to the ammonium zinc salt. As a matter of fact the solutions employed by Guyard, and those in which estimations are made by practical workers, do contain ammonium chloride formed in previous steps of the analysis. The proportion of zinc to phosphate suggested by Garrigues—1:5—is the amount of soluble phosphate necessary to turn red litmus blue after the zinc is precipitated. In order to find out whether the presence of so large an amount of the soluble phosphate is necessary in presence of ammonium chloride, the solution of zinc sulphate was precipitated in presence of the necessary amount of ammonium chloride by the microcosmic salt, in small excess above the equivalent of the ammonium phosphate, and the solution was made just ammoniacal to litmus with a few drops of dilute ammonia, both before and after heating, to convert it to crystalline condition. Experiment (15) shows that precipitation is not complete under these conditions. The zinc left in the solution was precipitated at once as sulphide, and estimated as the oxide, after dissolving in hydrochloric acid, and precipitating with sodium carbonate. In (16) of the table the first filtrate was treated with an excess of microcosmic salt and boiled. Another portion of the ammonium zinc phosphate was precipitated, and was filtered off and estimated. No zinc was found by sulphuretted hydrogen in the second filtrate.

From the results it seems obvious also that an excess of the soluble phosphate is necessary to complete the precipitation of the zinc as the ammonium-zinc phosphate, instead of partly ammonium-zinc phosphate and partly tribasic phosphate.

In Section E of Table III. are recorded results where the precipitation was made in presence of an excess of the precipitant either alone or in presence of ammonium chloride, the solution being made faintly acid to litmus with acetic acid, according to the manner in which Langmuir recommends to conduct the precipitation. All the results by the method are low. The condition of the ammonium-zinc phosphate most nearly approximating to the ideal is obtained, as shown in 9 to 14, by precipitating in presence of ammonium chloride in large amount. Microcosmic salt is added until the solution containing the ammonium salt is alkaline, and the whole is heated until the mass subsides in crystalline condition. The amount of ammonium chloride should be 20 grms. if the filtration is to be made as soon as the solution cools. One-half the amount will do if the liquid stands a number of hours. Larger amounts tend to give a salt too rich in

ammonia. The time of standing seems to be a less important factor than either the excess of microcosmic salt or ammonium chloride.

The Ammonium-cadmium Phosphate.

According to S. Drewsen ("Gmelin-Kraut," 6te Auflage, iii., 74), the cadmium-ammonium phosphate is precipitated by allowing a solution of cadmium sulphate to stand twenty-four hours with ammonium phosphate. It is very soluble both in acids and alkalis. No further preparation of this seems to have been recorded. For the work on this salt to be given below, made with reference to determining the constitution of the salt by hydrogen-sodium-ammonium phosphate, the effect of ammonium chloride in the precipitation, and the value of the salt for quantitative work, the solution of cadmium chloride employed was prepared as follows:—A solution of cadmium sulphate acidulated with hydrochloric acid was precipitated with sulphuretted hydrogen, filtered and washed, and the precipitated sulphide was dissolved in hydrochloric acid and filtered from possible traces of copper and lead. The solution of the sulphide in hydrochloric acid was boiled until all the sulphuretted hydrogen was expelled, and filtered on asbestos in a perforated crucible of platinum under pressure. The cadmium in the filtrate precipitated with ammonium carbonate in excess was washed free from chloride, dissolved in hydrochloric acid, and diluted to definite volume. It was standardised as oxide (Browning, *Am. Journ. Sci.*, xlv., 280) after precipitating with sodium carbonate with the necessary precautions.

The standard solution of cadmium chloride was drawn carefully from a burette into a platinum dish, and, while hot, was precipitated by adding hydrogen-sodium-ammonium phosphate until the solution was alkaline to litmus. After heating until the solution became crystalline, the whole stood three hours in case of 1 of Table IV. and sixteen hours in case of 2 and 3 before filtering. In Experiments 4 to 12 inclusive, recorded in the table, precipitation was made in the same manner as in 1 to 3 in presence of varying amounts of ammonium chloride, and the precipitates were filtered after standing as stated in Table IV. It is clear from the results that the cadmium separates out completely on long standing only. Moreover, the ideal condition of the ammonium-cadmium phosphate is obtained only when an abundance of ammonium chloride is present; but larger amounts of ammonium chloride dissolve this salt. In 14, where ammonia was added after precipitation was complete, the salt dissolved somewhat; also in 15, where the solution was left faintly acid with acetic acid, a large part of the salt was dissolved. These weights of cadmium dissolved in the filtrate were obtained by treating the filtrates with sulphuretted hydrogen, dissolving the sulphide in nitric acid, and weighing as oxide after precipitating with sodium carbonate.

The ammonium-cadmium phosphate is obtained in ideal condition by precipitating with microcosmic salt in presence of 10 grms. ammonium chloride in a total volume of 100 c.m. to 150 c.m. (shown in 6, 7, and 8, Table IV.), filtering after standing some time. On drying and igniting the pyrophosphate is left. Very large amounts of ammonium chloride (30 grms.) dissolve the salt, and seem to tend to cause the formation of a phosphate too rich in ammonia. Either acid or ammonia in small amount dissolves the salt, as is shown in 14 and 15.

The results of this investigation as to the analytical application of the double ammonium phosphates of beryllium, zinc, and cadmium may be summarised briefly as follows:—It is impossible to estimate beryllium with accuracy as the pyrophosphate obtained by igniting the double ammonium phosphate precipitated from beryllium solutions by microcosmic salt or ammonium phosphate in presence of ammonium chloride. In presence of the proper amount of ammonium chloride (10 grms. to 20 grms. in 100—200 c.m.³ of liquid) zinc-ammonium phosphate can be obtained in the ideal condition, which on

ignition yields the pyrophosphate. This method may serve, therefore, for the accurate estimation of zinc.

Cadmium may be estimated with accuracy as the pyrophosphate if the precipitate by microcosmic salt in the nearly neutral solution containing ammonium chloride in the proportion of 10 grms. to 100 c.c. is allowed to stand several hours before filtering. In this way all cadmium separates out from the solution as a beautiful crystalline mass of cadmium-ammonium phosphate of ideal constitution. The conditions must, however, be preserved with care; there must be no excess of ammonia, no free acid, and no excess of ammonium salt beyond the quantity indicated, while that amount is necessary.

THE OCCLUSION OF HYDROGEN BY METALLIC COBALT AND OTHER METALS.*

By GREGORY PAUL BAXTER.

(Concluded from p. 296).

The Occlusion of Hydrogen by Nickel.

THE study of the occlusion of hydrogen was extended to the case of a few other metals. The behaviour of nickel was found to be analogous to that of cobalt. According to Troost and Hautefeuille (*Comptes Rendus*, lxxx., 788) nickel in the form of ingots retains only traces of hydrogen, metal reduced from the oxide occludes maximum amounts and is pyrophoric, while electrolytic foil occupies a position between the two. The amount of occluded gas, according to their results, was equal in quantity to that obtained from cobalt, 100 volumes in the case of metal reduced from the oxide. Raoult (*Fahresb.*, 1869, 272) states that very porous nickel, if used as the negative pole of a voltameter, takes up 165 volumes of hydrogen, the greater part of which is given off at ordinary temperatures in the air. These high results are contradicted by those of Neumann and Streintz (*Monatsh. Chem.*, xii., 642), who found about 17 volumes of gas in metal reduced from the oxide, and by those of Richards and Cushman (*Proc. Am. Acad.*, xxxiv., 333), who found only 8 volumes in the purest metal obtained from the same source.

The lesser values are supported by the following analyses performed with material kindly furnished by Dr. Cushman, and known to be free from every impurity. In Analyses I. and II. the nickel was subjected to combustion immediately after reduction. The oxide from Analysis I. was reduced, and the resulting metal evolved no hydrogen in a vacuum, as was shown by the water yielded upon subsequent oxidation (Analyses III. and IV.). When heated in a vacuum the metal lost nearly all its occluded hydrogen (Analysis V.). Like cobalt, nickel which had been heated to a high temperature during reduction sintered together and lost its power to occlude (Analysis VI.). Finally, material reduced from the bromide occludes no hydrogen (Analysis VII.), as has already been shown by Richards and Cushman (*Proc. Amer. Acad.*, xxxiv., 333).

I. 5.7 grms. of nickel yielded 0.0033 grm. of water, or 5.7 volumes of hydrogen.

II. 4.0 grms. of nickel yielded 0.0010 grm. of water, or 2.1 volumes of hydrogen.

III. 5.7 grms. of nickel yielded 0.0060 grm. of water, or 10.7 volumes of hydrogen.

IV. 5.7 grms. of nickel yielded 0.0057 grm. of water, or 10.2 volumes of hydrogen.

V. 5.7 grms. of nickel yielded 0.0017 grm. of water, or 2.9 volumes of hydrogen.

VI. 6.0 grms. of nickel yielded 0.0006 grm. of water, or 1.0 volume of hydrogen.

VII. 1.5 grms. of nickel yielded 0.0001 grm. of water, or 0.7 volume of hydrogen.

* Contributions from the Chemical Laboratory of Harvard College. From the *American Chemical Journal*, Vol. xxii., No. 5, Nov., 1899.

Manifestly nickel is subject to the same influences as cobalt. The large amounts of hydrogen obtained by other experimenters can be explained by the fact that their material was very impure. Impure nickel and cobalt in the same state of minute subdivision apparently possess the property of retaining hydrogen to the same degree. Pure nickel, owing to its lower melting-point, should sinter more readily than pure cobalt. The lesser relative surface thus offered is probably the reason for the smaller amounts of occluded gas.

The Occlusion of Hydrogen by Copper.

The occlusion of hydrogen by copper has already been the subject of numerous researches which gave widely varying results (Graham, *Fahresb.*, 1866, 50; Thudichum and Hake, *Fourn. Chem. Soc.*, 1876, xxxiii. [2], 251; Johnson, *Fourn. Chem. Soc.*, xxxv., 235; Neumann and Streintz, *Monatsh. Chem.*, xii., 642; Richards, *Proc. Am. Acad.*, xxvi., 292; and others). One main fact stands out in all these investigations. Where the copper was known to be pure the occlusion was very slight, whatever the source of the copper.

Very pure cupric oxide, made by evaporation of a solution of electrolytic copper in pure nitric acid, and ignition of the residue, after reduction, yielded a very small amount of water (Analyses I., II., III., and IV.). In a vacuum at ordinary temperatures the hydrogen was retained (Analysis V.), but after ignition in a vacuum a negligible amount of water was found (Analysis VI.).

I. 2.5 grms. of copper yielded 0.0003 grm. of water, or 1.5 volumes of hydrogen.

II. 5.1 grms. of copper yielded 0.0009 grm. of water, or 2.1 volumes of hydrogen.

III. 5.1 grms. of copper yielded 0.0010 grm. of water, or 2.3 volumes of hydrogen.

IV. 5.1 grms. of copper yielded 0.0009 grm. of water, or 2.1 volumes of hydrogen.

V. 5.1 grms. of copper yielded 0.0008 grm. of water, or 1.8 volumes of hydrogen.

VI. 5.1 grms. of copper yielded 0.0003 grm. of water, or 0.7 volume of hydrogen.

The Occlusion of Hydrogen by Silver.

Silver reduced from the oxide takes up minimum amounts of hydrogen, if any.

I. 2.5 grms. of silver yielded 0.0001 grm. of water, or 0.5 volume of hydrogen.

II. 2.5 grms. of silver yielded 0.0005 grm. of water, or 2.8 volumes of hydrogen.

III. 5.0 grms. of silver yielded 0.0003 grm. of water, or 0.8 volume of hydrogen.

This result is in accordance with the results of Graham (*Fahresb.*, 1866, 51), whose silver wire occluded 0.2 its volume of the gas, while his metal, obtained by reduction of the oxide, yielded 0.9 its volume. Neumann and Streintz found no hydrogen in their silver reduced from the oxide (*Monatsh. Chem.*, xii., 642).

It is noteworthy that in all the work performed upon the occlusion of hydrogen by the four metals, cobalt, nickel, copper, and silver, when they were reduced from pure oxides at low temperatures, the magnitude of the occlusion varied with the fusion-points of the metals. Cobalt, whose melting-point is the highest, occludes by far the greatest volume of gas, while silver, which melts at the lowest temperature, occludes minimum quantities. The explanation of this peculiarity has already been mentioned. The sintering or fusing together of the metals is greater, the nearer the reduction temperature is to their melting-points, while the surface offered, which determines the amount of occlusion, diminishes with the amount of sintering. Since the melting-points of copper and silver are very near together, one would expect their power of occlusion to be very nearly the same, as is the case.

Pure ferric oxide is not reduced to any considerable extent by hydrogen at the low temperature employed in the case of the four preceding metals. When a temperature

sufficiently high to produce reduction is employed, no appreciable amounts of hydrogen are occluded, because of sintering of the metal. On account of this difficulty no work could be done with iron which would be comparable with that done with the other metals.

The question as to the formation of compounds of the metals with hydrogen, similar to "Hydrogenium," is not easily settled. On the one hand, the fact that the quantity of occluded gas varies with the surface presented seems to point to simple condensation on the surface, as in the case of charcoal; on the other hand, the pertinacity with which the hydrogen is retained in a vacuum when cold is evidence in the other direction. For the present this point must needs remain undecided.

A word can be profitably said here in regard to the use of the terms "occlusion" and "adsorption." In its stricter sense the word "occlusion" should be confined to an intimate combination, such as that of palladium with hydrogen. "Adsorption," on the other hand, refers to simple condensation or concentration in the immediate vicinity of a given surface. Owing to the doubt as to the nature of the process by which the hydrogen is retained by the metals considered, the question as to the designation of the process is necessarily unsettled, but Graham's word has been usually employed above.

In conclusion, I wish to express my thanks to Professor Theodore William Richards for much advice and encouragement given during the course of this work.

DIRECTIONS FOR CERTAIN ALKALOIDAL ASSAYS.

By H. M. GORDIN and A. B. PRESCOTT.*

A GENERAL METHOD FOR THE EXTRACTION OF ALKALOIDS IN ASSAYS.

(NOTE.—Analytical results in support of these directions are given in an accompanying paper, "Further Work upon the Estimation of Alkaloids and the Assay of Alkaloidal Drugs," presented in this Association at this date. Also in the paper entitled, "Certain Alkaloidal Periodides, and the Volumetric Estimation of Alkaloids as Higher Periodides," by the same authors, *Proc. Am. Phar. Assoc.*, 1898, p. 340; *Pharm. Arch.*, I. p. 121; *Fourn. Am. Chem. Soc.*, 1898, p. 724. A paper on Hydrastine Hexiodide and Assay of Hydrastis, *Am. Journ. Pharm.*, 1899, p. 257. Further, see the article, "The Periodides of the Alkaloids as Molecular Forms for Estimation," &c., by A. B. Prescott, 1897, *Pharm. Review*, vol. xv., and other papers since 1895).

I.—AS A METHOD BY PERCOLATION.†

One to four grms. of the finely powdered drug is weighed into a low wide-mouthed vessel, with a round bottom, holding eight or ten ounces, and having a well-fitted cork, such as a screw-top ointment jar (an ordinary tea cup fitted with a specie cork answers well). The powder is rubbed up with a small pestle to a fine paste by adding a little of a solvent mixture, composed of stronger ammonia water and alcohol, each 5 c.c., chloroform 10 c.c., and ether 20 c.c.‡ Then a few more c.c. of this mixture are added, so as to have the drug well covered with the liquid, using in all about five times the amount of the drug taken. The vessel is corked, with the pestle inside, and is set aside for about four or five hours, taking care to agitate by circular movement very frequently during that interval.

* In the Work of Research Committee D., Section 2, Committee on Revision and Publication of the Pharmacopœia of the United States, 1890—1900. Read before the American Pharmaceutical Association, September, 1899.

† These directions were published, nearly as here given, by the authors, in an article, "Emetine Octiodide," &c., *Pharm. Review*, vol. xvii., 1899. This general method is not applicable to ipecacuanha. See under "Assay of Ipecacuanha" further on.

‡ In the case of Hydrastis canadensis the chloroform is replaced by an equal volume of ether.

After that time the cover is removed, and the vessel kept in a current of air, stirring frequently till all odour of ammonia has disappeared. With a good draught and frequent stirring the powder will be almost perfectly dry in about one hour. The vessel is then put into a vacuum desiccator over sulphuric acid for about four or five hours.

An amount of powdered sodium chloride,* equal to about five or six times the amount of drug employed, is then carefully mixed in, with use of the pestle, and the whole thrown into a small percolator, one provided with a glass stop-cock, and having a plug of cotton at the bottom. (A suitable percolator is easily made out of an ordinary piece of glass tubing fitted with a perforated cork, through which passes a tube having a glass stop-cock).

The vessel is then cleaned out several times with small quantities of sodium chloride, and the cleanings added to the percolator. The mixture in the percolator is then covered with a little of the cotton, which is pressed down with a piece of glass, and a suitable menstruum, usually chloroform, is poured slowly into the percolator till the menstruum reaches the stop-cock. The latter is then closed, the percolator covered and set aside for five or six hours. After that time the stop-cock is opened, and the drug exhausted with the menstruum, percolating until ten drops of the percolate being evaporated on a watch-glass, and the residue taken up with a few drops of acidulated water, the solution shows no turbidity whatever on adding a few drops of the solution of iodine. When finished, the percolate, which is received in a flat evaporating dish, is placed in a good draught at a temperature of about 30° C. When the liquid is reduced to a very small volume 10 c.c. of acidulated water† are added, and then a few c.c. of ether, or petroleum ether, so as to have an ethereal liquid cover the aqueous solution,‡ when the whole is stirred with a glass rod until all the ethereal liquid is driven off. The liquid is then filtered, and the evaporating dish and filter washed several times with acidulated water. In this way is obtained a colourless solution of the alkaloid, which can be worked up for any method of estimation.§

II.—AS A HOT EXTRACTION METHOD.

Instead of the cold percolation, as above directed, hot extraction in any suitable apparatus may be used, all other features of the operation being the same. If a Soxhlet tube is used care should be taken that the syphon works intermittently, as otherwise the extraction is very incomplete; if Dunstan and Short's apparatus (*Pharm. Journ.* [3], xiii., 664) is used, the boiling of the solvent should be so regulated as to have always a layer of about 2 c.m. of it on the top of the drug. Our experience has taught us that for quantitative work cold extraction by percolation requires less skill and care than hot extraction in a Soxhlet tube, though with careful operation the latter method is preferable.

THE VOLUMETRIC ESTIMATION OF ALKALOIDS BY PRECIPITATION WITH FREE IODINE.||

Estimation by Formation of a Periodide, so far Applied to Atropine, Morphine, Strychnine, Brucine, Emetine, Hydrastine, and Caffeine.

For opium assay see *prox.*

* In the case of hydrastis the sodium chloride is replaced by barium nitrate.

† If an alkalimetric assay is intended, the acidulated water in the operation should be closely standardised and taken in definite quantities.

‡ If the menstruum is all evaporated off it is sometimes difficult to dissolve out the alkaloids with the acidulated water. If chloroform be used, coming below the aqueous layer, it evaporates too slowly.

§ The method of extraction described above presents particular advantage in those cases where several alkaloids soluble in different menstrua are present in the drug, as by using these menstrua successively a separation of the alkaloids can be easily effected. This principle we have applied to the assay of opium, and to that of *Hydrastis canadensis*.

|| These directions were given in substance in an article entitled "Emetine Octoiodide and the Estimation of Alkaloids Generally," by the authors of this paper, in *Journ. Am. Chem. Soc.*, xxi., p. 234, March, 1899; *Pharm. Review*, vol. xvii., 1899.

For assay of *nux vomica*, with separation of strychnine from brucine, see *prox.*

For assay of *ippecac.*, see *prox.*

For estimation of berberine in assay of *hydrastine*, see *prox.*

For estimation of caffeine the alkaloidal solution must be invariably acidulated (Gomberg, 1896). For assay of *kola*, see Knox and Prescott, 1896-7, *Proc. Am. Phar. Assoc.*, xlv., p. 128, and xlv., p. 131; *Journ. Am. Chem. Soc.*, xix., p. 63; xx., p. 34.

The Reagents and Utensils Required in the Volumetric Work.

(1) A standardised solution of iodine dissolved in water with iodide of potassium to be of about decinormal strength (12.653 grms. of free iodine in 1000 c.c.). The solution may be made as the volumetric test solution of iodine of the U.S.P., and used with the exact decinormal factor of iodine if preferred.

(2) A solution of sodium thiosulphate, of about decinormal strength, standardised to known ratio with the iodine solution. The volumetric test solution of thio-sulphate of the U.S.P. may be used.

(3) The starch test solution of the pharmacopœia.

(4) The burettes and centesimal measuring vessels for any volumetric work in analysis.

THE VOLUMETRIC OPERATION.

The final alkaloidal solution obtained by whatever mode of extraction,* but always representing a definite quantity of the drug to be assayed, is poured slowly and with constant stirring into a flask holding 100 c.c., in which has been previously drawn 20 or 30 c.c. of the standardised solution of iodine, and 1 or 2 c.c. of dilute hydrochloric acid† (U.S.P.). The flask is then filled up to 100 c.c., stoppered, and well shaken till the periodide has separated out. The supernatant liquid is to be perfectly transparent, but of a red iodine colour. Fifty c.c. are then filtered off, and in this portion the excess of iodine determined by means of standard sodium thiosulphate. The amount of iodine consumed, multiplied by the proper factor, gives the amount of alkaloid present in the quantity of drug taken. (For example: If operating upon 2 grms. of powdered *ippecac. root*, the iodine consumed be 0.957764, then the percentage of emetine in the drug equals $0.957764 \times 0.55 \times 100/2 = 2.63$).

In case more than one alkaloid be present in the drug a mean iodometric factor can be drawn, as shown for strychnine and brucine in the list of factors. In alkalimetric estimations a mean factor is often used in assay for total alkaloids, and the same is equally justifiable in iodometric work when the data are known.

Should there be no precipitate with iodine, but only a slight turbidity, then the drug is extremely poor, and for the assay a much larger quantity than has been used should be taken. On the other hand, should the supernatant liquid, after adding the alkaloidal solution to the solution of iodine, and separating the periodide by shaking, have very little colour, or be almost colourless, then it is certain that the drug is very rich, and either a smaller quantity of the drug or a larger quantity of the iodine solution must be employed in the assay.

Generally, if the drug contains as much as 3 per cent of alkaloid 1 gm. should be taken for the assay; if it contains less than the above amount, but not less than two-tenths of 1 per cent of alkaloid, then a quantity between 1 and 5 grms. should be taken.

* Directions for extraction are given further on. Other procedure for extraction is given in Lyons' "Handbook of Assaying," 1899, Detroit: Nelson, Baker, and Co., pp. 26-30.

† It is always to be remembered that this estimation by formation of higher periodides requires the alkaloid to be added slowly to the iodine with excess of the latter. Except in the case of morphine an excess of acid is not hurtful, and even promotes the separation of the periodide. Hydrochloric is to be preferred to sulphuric acid.

The Iodine Factors.

The precipitate formed.	Quantity of alkaloid to 1'0000 of iodine consumed.	Quantity of alkaloid to 1 c.c. of tenth-normal solution of iodine.(a)
Atropine, $C_{17}H_{23}NO_3 \cdot HI \cdot I_8$..	0'285	0'00361
Morphine, $C_{17}H_{19}NO_3 \cdot HI \cdot I_3$..	0'749	0'00948
Strychnine, $C_{21}H_{22}N_2O_2 \cdot HI \cdot I_6$	0'439	0'00556
Brucine, $C_{23}H_{26}N_2O_4 \cdot HI \cdot I_6$..	0'513	0'00655
Mean of strychnine and brucine	0'478	0'00605
Emetine, (b) $C_{28}H_{40}N_2O_5 \cdot HI \cdot I_7$	0'55	0'006
Hydrastine, $C_{21}H_{21}NO_6 \cdot HI \cdot I_5$	0'604	0'00764
Caffeine, $C_8H_{10}N_4O_2 \cdot HI \cdot I_4$..	0'383	0'00485

(a) If the analyst prefers to standardise his volumetric solution of iodine to exact decinormal strength, or to adjust the consumption of iodine to this strength by use of a correcting factor, then he will multiply the c.c. of iodine solution consumed by the proper factor in this column. (1 c.c. decinormal solution contains 0'012653 grm. of iodine). The more simple way, however, is to register the actual quantity of iodine in 1 c.c. of the solution, be the same above or below the 0'012653 grm., and multiply this actual quantity by the number of c.c. used up, so as to get the *weight* of iodine consumed. This, multiplied by a factor of the first column above, gives the quantity of alkaloid estimated in grammes.

(b) That is a provisional representative of the total alkaloids of ipecacuanha.

THE ASSAY OF OPIUM.

The Extraction of the Morphine and its Volumetric Estimation either by Standardised Solution of Acid or by Standardised Solution of Iodine.

(This method of assay with the iodometric estimation appeared in its primary form, with the analysis of morphine tetraiodide, &c., in an article by the present authors, in June, 1898 (*Pharm. Archives*, i., p. 121), and with some additions in *Proc. Am. Pharm. Assoc.*, 1898, p. 340; also in *Journ. Am. Chem. Soc.*, 1898, p. 724. The directions, with adaptation to the alkalimetric way of estimation, as here given, formed a part of "The Assay of Opium: a Supplementary Note" in the *Pharmaceutical Review*, xvii., 1899, and to appear in the *Archiv der Pharmacie*).

For the use of *hot extraction instead of cold percolation* in treatment of the opium in this process, see an article entitled "Further Work upon the Estimation of Alkaloids," in which also are included a few results in comparison with the U.S.P. method, and a brief discussion of the subject.

The Materials and Utensils for the Assay.

Opium in very fine powder. Powdered sodium chloride, such as is used for the table. An ethereo-ammoniacal mixture composed of stronger ammonia water (U.S.P.) and alcohol, of each 5 c.c.; chloroform (U.S.P.), 10 c.c.; and ether, 20 c.c. Benzol boiling at about 80° C. A mixture of one volume of absolute alcohol and five volumes of chloroform. Twentieth normal sulphuric acid and twentieth normal potassium hydrate solution. Neutral methyl-orange paper. Standard solution of iodine, of any known strength in the neighbourhood of 1 per cent, and standard solution of sodium thiosulphate of about twentieth normal strength.

A 4 or 6 ounce screw-top ointment jar, having a bottom concave within. A small pestle, just long enough to rest half upright within the jar when it is closed. A small glass percolator provided with a stopcock, and of the length of about 22 c.m. and inner diameter of about 1'3 c.m. (the lower part of a burette cut in two answers very well).

Directions for the Assay.

Weigh out 3 grms. of the opium into the ointment jar, rub it up by means of the pestle with a few c.c. of the ethereo-ammoniacal mixture to make a fine paste, taking care not to smear the sides of the jar unnecessarily, then

add about 2 c.c. more of the same mixture, so as to have the opium well covered with liquid, screw down the top, leaving the pestle inside, and set the jar aside for five or six hours. After that time the jar is opened, about 10 grms. of the sodium chloride thoroughly mixed in with the opium, and the open jar placed in a good current of air, stirring frequently with the pestle in order to prevent formation of lumps. In about an hour the powder will be nearly dry. The jar is then placed in a vacuum desiccator containing, besides sulphuric acid, a vessel of paraffin, and left there over night. The jar is then taken out, any lumps in the powder carefully crushed with the pestle, and the mixture transferred first to the glazed paper, and then to the percolator, in the bottom of which a plug of cotton has been placed. The jar is rubbed out several times with small quantities of the sodium chloride, the rinsings added to the percolator, and, having placed a plug of cotton and a piece of glass on the top of the powder, the opium is extracted with benzol by percolating very slowly, until, upon evaporating ten drops of the percolate on a watch-glass, and taking up the residue with ten or twelve drops of very slightly acidulated water, no turbidity appears by the addition of two drops of the iodine test solution. After the narcotine, thebaine, codeine, and most other alkaloids have in this way been completely removed by the benzol, the receiver is taken away (the benzol, of course, can be recovered by distillation, and used over and over again), and a shallow evaporating dish placed under the percolator.

The percolation is now continued slowly with the mixture of alcohol and chloroform (see Burg., *Zeit. Anal. Chem.*, xix., p. 222) until ten drops of the percolate tested as above give no reaction for alkaloids. The evaporating dish is now put into a good current of air and left over night, or until the solvent has disappeared. (This makes the whole assay occupy about two days and two hours if it be started in the morning). The bottom of the dish will then be found to be covered with a good crop of crystals intermixed with a little resinous matter.

Estimating in the Alkalimetric Way.

Fifty c.c. of the twentieth normal sulphuric acid are now carefully run out from a burette into the evaporating dish, the contents rubbed well with a pestle till everything is detached from the bottom and sides of the dish, and then, without filtering, poured into a tall narrow measuring cylinder. The dish is then carefully washed several times with small quantities of water, the washings added to the cylinder, and the latter filled up to make 90 c.c. After shaking well a few minutes, and setting aside till solid particles have settled down (the filtration is much accelerated if the waxy particles are prevented from entering the filter), 75 c.c., representing $2\frac{1}{2}$ grms. of the opium, are filtered off into a beaker holding some 250 or 300 c.c., about 50 c.c. of water added, and then 35 or 40 c.c. of the twentieth normal potassium hydrate run out from a burette into the beaker. Twentieth normal sulphuric acid is now carefully added, 1 c.c. at a time, stirring with a glass rod, and testing the liquid after each addition by immersing for about fifteen seconds small strips of neutral methyl-orange paper. As soon as the paper becomes reddish, 1 c.c. of the potassium hydrate solution is added, and then again of the sulphuric acid, adding now one-tenth of a c.c. of the latter at a time, till the paper becomes reddish. In order to get exact results, the acid and alkali solutions should be standardised in nearly the same conditions under which the titration of morphine takes place; that is, using about 175 c.c. of liquid, and noting the appearance of the reddish tint upon the test-paper at the point of neutrality. The strips of reagent paper should, of course, be wet with the wash-bottle before immersion in the beaker. Though the solution of morphine has a yellow colour from some extractive matter, so that the end reaction cannot be found by adding a liquid indicator to the solution, there is not the slightest difficulty in noting

the appearance of the reddish tint upon the cream-coloured methyl-orange paper. Of course other indicators, like iodo-eosin in ethereal solution, &c., might be found to give equally good results; but having found the dip-test with methyl-orange paper to give sharp and definite results with this alkaloid, we have not experimented upon other indicators.

One c.c. of twentieth normal acid being equivalent to 0.0142 grm. anhydrous morphine, the number of c.c. of the acid consumed by the alkaloid from $2\frac{1}{2}$ grms. opium, multiplied by 0.568 ($=0.0142, 100/2.5$), gives the percentage of morphine in the opium.

Estimating in the Iodometric Way.

When it is desirable to control the alkalimetric assay with an iodometric one, the contents of the beaker are emptied in a 250 c.c. measuring flask, washing the beaker two or three times with small quantities of water, the flask filled up to 250 c.c., about 3 or 4 grms. calcium hydrate added, and the mixture shaken for about an hour. This treatment removes a good deal of the colouring matter, but keeps the morphine in solution. 50 c.c., which represent half a grm. of opium, are now filtered off into a 100 c.c. flask, and the liquid slightly acidified with hydrochloric acid. The liquid will now be only slightly coloured, 20 c.c. of the standard iodine are now run out from a burette into the flask, the latter filled up to 100 c.c., and the flask well shaken till the supernatant liquid becomes perfectly transparent, but has a dark red iodine colour.* 50 c.c. are now filtered off, and the excess of iodine determined by the standard sodium thiosulphate, using starch as indicator. The amount of iodine consumed by the half grm. of opium, multiplied by 149.8 ($=0.749 \times 100 \times 2$),† gives the percentage of morphine in the opium.

If only an iodometric assay be desired but 1 grm. opium need be taken for the assay, and the latter conducted exactly as described above up to the point where the chloroform alcohol has been removed by evaporation. At this point the residue is taken up with good lime water by rubbing the evaporating dish thoroughly with it, pouring the mixture in a 100 c.c. flask, filling the latter up with lime water to make 100 c.c., shaking the flask about an hour, filtering off 50 c.c. into another 100 c.c. flask, acidulating, and then finishing up as above.

THE ASSAY OF NUX VOMICA.‡

The acidulated water solution of the total alkaloids of the drug, as obtained by the directions on page given above, or other mode of extraction, is made up to a definite volume, say 100 c.c. If 4 grms. of the drug have been taken, then 25 c.c. will represent 1 grm. of the drug, and will be sufficient for one estimation. This volume, then, is run from a burette into a 100 c.c. flask in which has been placed 20 c.c. of the decinormal iodine solution and 2 c.c. dilute hydrochloric acid, when the amount of iodine consumed by the total alkaloids in that 1 grm. of nux vomica is reached in the way described above. Let that amount be a . If only the amount of total alkaloids in the nux vomica is desired, it is sufficient to multiply a by 47.8, which is equal to 100 times the mean factor of strychnine and brucine, and the percentage of total alkaloids is at once obtained.

For the Separate Estimation of Strychnine and Brucine a modification of Dunstan and Short's§ method of separation by ferrocyanide, we have found to work fairly well as follows:—Another portion of the alkaloidal solution, representing 2 grms. of the nux vomica, that is 50 c.c., is

run out from the burette into an Erlenmeyer flask of the capacity of about 300 c.c., and to the contents of the flask 10 c.c. of a 2 per cent solution of sulphuric acid is added, and then water enough to make in all about 200 c.c. Then pour in 25 c.c. of a 5 per cent solution of potassium ferrocyanide, stopper the flask, and shake continuously for about half an hour. Now filter, wash the precipitate on the filter repeatedly with water containing 1 per cent of sulphuric acid till a few drops of the filtrate diluted with a little water have no bitter taste. The filter is then pierced, and the precipitate rinsed with use of the wash-bottle into a 100 c.c. flask. To the contents of the flask are then added 20 c.c. of a 5 per cent solution of zinc sulphate, and the flask kept on a boiling water-bath for about fifteen minutes. The zinc sulphate decomposes the strychnine ferrocyanide, zinc ferrocyanide is precipitated, and strychnine sulphate remains in solution. The flask is then completely cooled, and water enough added to make 100 c.c. Of this 50 c.c.—representing again 1 grm. of the nux vomica, but deprived of the brucine—are then filtered off, and run out from the burette into a 100 c.c. flask containing 20 c.c. decinormal iodine solution and about 2 c.c. of dilute hydrochloric acid. The amount of iodine consumed by the strychnine alone is then determined as above. Let it be b . Then $b \times 43.9$ (100 times the strychnine factor) gives the percentage of strychnine, and $(a-b) \times 51.8$ is the percentage of brucine in the nux vomica.

To test the exactness of this method, we prepared a solution containing known quantities of each of these alkaloids, and determined the same by the described method. The results, as can be seen from the following statement, are fairly satisfactory, if we consider the well-known difficulties of this separation. The solution contained 0.16 per cent strychnine and 0.22 per cent brucine (anhydrous).

	Iodine consumed by 10 c.c. before the removal of brucine.	Iodine consumed by 10 c.c. after the removal of brucine.	Found.		Contained.	
			Strychnine.	Brucine.	Strychnine.	Brucine.
1.	0.0843132	0.032397	0.14	0.24	0.16	0.22
2.	0.0843130	0.032397	0.14	0.24	0.16	0.22

ASSAY OF IPECACUANHA.

For extraction of the drug use one of the methods given in Lyons' "Assaying" (Detroit, 1899). The cold percolation process of extraction previously directed as already remarked, does not work well with this drug.

Ether, chloroform, and acetone were tried as menstrua in the cold percolation, but the results were too low. The ammoniated mixture fails to yield all the alkaloid. This possibly explains why Flückiger (Pharm. Zeitung, 1886, p. 30), extracting by ammoniated chloroform, obtained exceptionally low results (See also Guareschi, Alkaloide, 1896, p. 527).

In iodometric estimation the total acidulated alkaloid solution is made up to a definite volume, an aliquot portion taken, and added to a measured excess of the iodine solution, as directed heretofore. The iodine factor of emetine is taken as fairly near the mean factor of the total alkaloids.

ASSAY OF HYDRASTIS.

In the assay of *Hydrastis canadensis*, for berberine and for hydrastine, the Directions for the Assays are given in an accompanying article entitled "Further Work upon the Estimation of Alkaloids," &c. In the plan of the assay the hydrastine is dissolved with absolute ether, and estimated iodometrically, as a hexaiodide. The berberine, undissolved by the absolute ether, is estimated volumetrically by precipitation as berberine hydriodide, the excess of the precipitant, potassium iodide, being determined by silver nitrate with sulphocyanate. But before the berberine is precipitated as hydriodide, it is separated in its acetone compound. And before the alkaloids are acted

* See our article in *J. Am. Chem. Soc.*, 1898, p. 722; *Proc. Am. Pharm. Assoc.*, 1898, p. 368.

† 0.75 is here taken instead of 0.74914, which is the factor for morphine (*loc. cit.*, p. 724).

‡ From an article by the authors in *Pharm. Review*, xvii, 1899.

§ *Pharm. J. Trans.* (3), xiv., 290; *Am. J. Pharm.*, 1883, 579. Any other method of separation of strychnine and brucine may be used with the iodometric estimations.

upon by the reagents, they are liberated from the powdered drug by maceration with an ethereo-ammoniacal mixture.

CORRESPONDENCE.

LABORATORY LAMP.

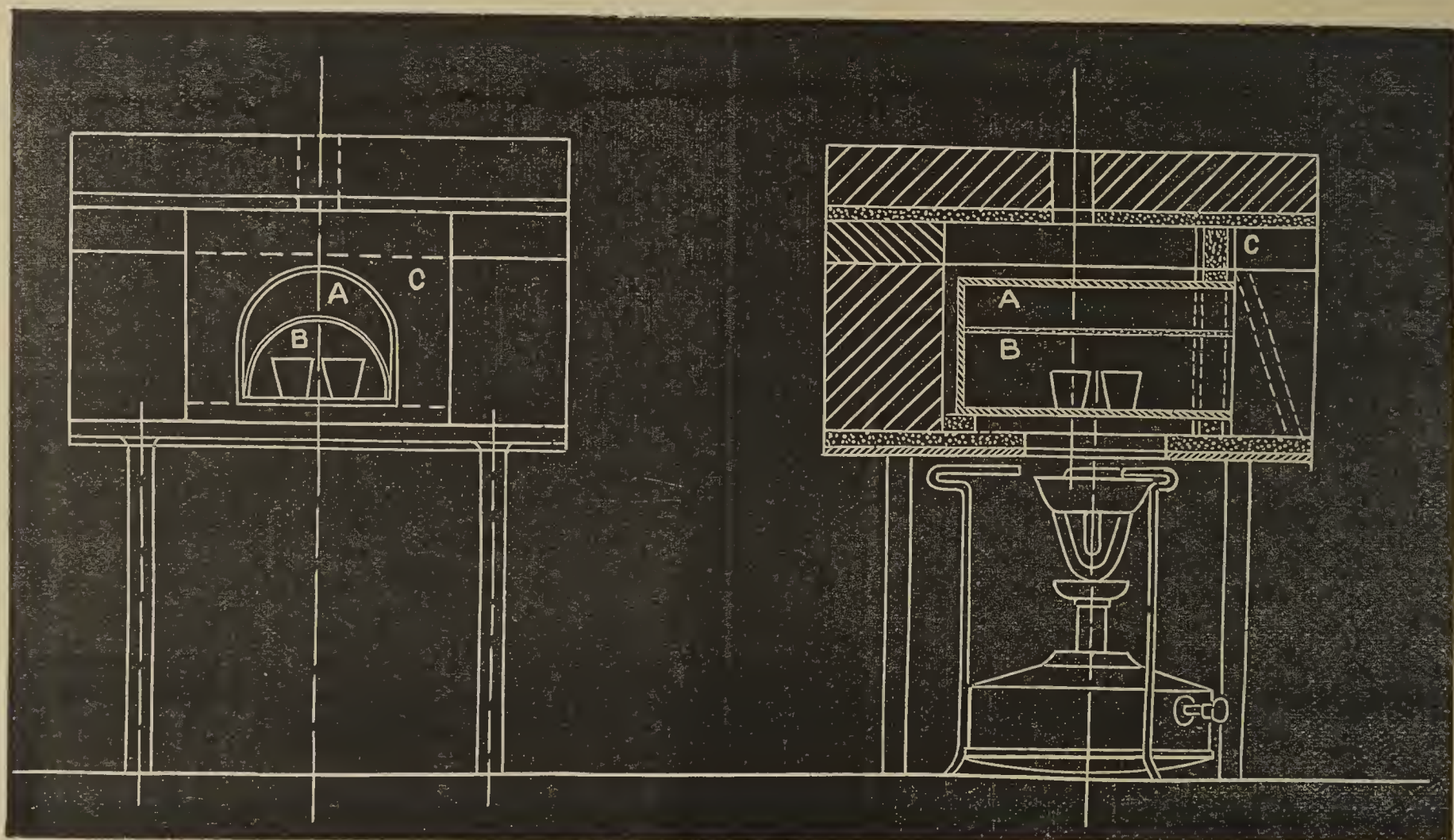
To the Editor of the Chemical News.

SIR,—Seeing that Prof. Frank Clowes has replied to "Chemicus," and that he suggests the use of a methylated spirit lamp arrangement, and, as this may be too expensive for him, I herewith send a drawing of my arrange-

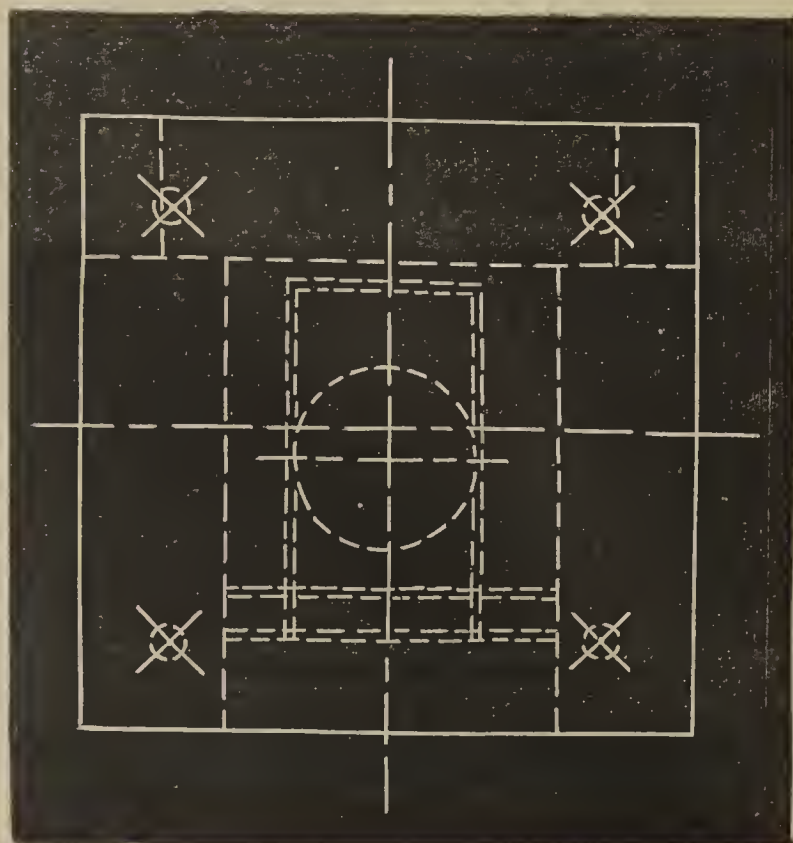
ment of a (Swedish) petroleum lamp, with a muffle furnace of simple construction, which I find very efficient and cheap in the determination of the ash of coal, coke, yeasts and beer, and water residues.

On lighting up lamp, and placing it in position shown under muffle, in ten minutes more than half of the bottom of muffle is heated to a red heat; on introducing four samples of about 2.5 grms. of coal in porcelain crucibles, in from ten to fifteen minutes all the volatile matter is evolved, and in three hours' time the weights of ash are constant. This is less time than I can do same quantities in a Fletcher's gas-heated muffle furnace, and only with a consumption of petroleum 0.797 at the rate of 6 ozs. by vol. per hour.

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Montpelier Hill, Dublin.

RELATIONS BETWEEN THE ATOMIC WEIGHTS AND PHYSICAL PROPERTIES OF ELEMENTS.

To the Editor of the Chemical News.

SIR,—Mr. Bayley's note in your issue of the 15th inst. (CHEM. NEWS, vol. lxxx., p. 282) seems to have a defect, and that is, if the formula melting-point (absolute) \times coefficient of linear expansion gives a constant for some elements, why should it not do so for all?

To take a universal absolute zero as -273° C. can lead to many misunderstandings. That this temperature should have the properties attributed to absolute zero is, in the light of our present knowledge, impossible, and the title is only a survival from the infancy of modern chemistry.

If the two cubes of Zn and Cd, mentioned by Mr. Bayley, were of the same volume at absolute zero, they would be

of the same volume at their respective melting-points, but the absolute zero for each would differ. Therefore, in the cases given, the coefficients of expansion (taken presumably at similar temperatures) are multiplied by ranges of temperature not similar, and thus the constant obtained may be due to chance.

More likely, the coefficient of expansion, taken in each case at a temperature similarly located between the melting- and boiling-points, multiplied by the range of temperature between the melting- and boiling-points, would give a more universal constant.—I am, &c.,

ALFRED WERTHEIMER.

Stirling Chemical Works,
Stratford, E., Dec. 26, 1899.

REMINISCENCES OF BUNSEN.

To the Editor of the Chemical News.

SIR,—In Mr. Bolton's interesting Reminiscences of Bunsen (CHEMICAL NEWS, lxxx., 283), he mentions the fact of Bunsen touching a quantitative precipitate, and his washing it off Bunsen's thumb.

Forty-six years since I remember Dr. Medlock telling me a similar tale, the only difference being that the one who touched the precipitate, and used the same words as Bunsen, being a petty German Prince who was visiting the laboratory, and the one who used the wash-bottle being Liebig.

The Prince, I think, would be more likely to touch the precipitate than Bunsen, from the latter's instinct as a chemist, even although he may have been an "Absent-minded Beggar."—I am, &c.,

E. B.

December 19, 1899.

OBITUARY.

JOHN FREDERICK HODGES.

It is with regret that we record the death of Prof. John Hodges, M.D., J.P., of Queen's College, Belfast, which took place on December 13th at the ripe age of eighty-four years.

The name of Prof. Hodges has been identified with Belfast for more than a generation, but the news of his death will cause a feeling of sorrow extending beyond the limits of the city in which it occurred.

John Frederick Hodges was born in County Down, and early entered the medical profession. He studied at Glasgow University, and in the year 1837 he became a Licentiate of the Faculty of Physicians and Surgeons. Shortly afterwards Dr. Hodges entered upon a general medical practice at Downpatrick. He had, however, always manifested a strong taste for chemistry, and having, while at Glasgow, come under the influence of the celebrated Graham, and also having his attention drawn to the researches of Liebig, he decided upon devoting himself entirely to the pursuit of chemical science. He therefore abandoned his practice and proceeded to Germany, where he studied at the University of Giessen. This entirely changed his subsequent career, and on his return home he devoted himself solely to chemistry, more especially in its bearing upon agriculture—a subject in which he acquired a high reputation.

Dr. Hodges succeeded Dr. Andrews as Lecturer on Chemistry in the old Belfast College, and on the foundation of the local Queen's College he was appointed Professor of Agriculture and also Lecturer on Medical Jurisprudence. He was a Fellow of a number of scientific societies, and held many appointments, besides being the author of a number of works on chemistry. He was

married and had a large family, some of whom have already distinguished themselves in various fields.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxix., No. 23, December 4, 1899.

Compound Metallic Radicles. Mercury Derivatives.—M. Berthelot.—The author has measured the heat of formation of three mercury-derived radicles—mercury dimethyl, mercury diethyl, and mercury diphenyl.

Lactic Acid.—MM. Berthelot and Delépine.—Lactic acid and its nitrogen and other derivatives play an essential part in all investigations relating to animal heat. Their heats of combustion and formation are imperfectly known, only having been determined by an indirect calculation and by an approximate numerical relation, deduced from numbers obtained not from the acid or its salts, but from its ether. The authors have re-determined the numbers in three different ways—by means of silver lactate, zinc lactate, and a lactide, a very important anhydride, on account of its constituting with glycolide the prototypes of the anhydride of the alcohols of the acids.

Explosion of Potassium Chlorate.—M. Berthelot.—Potassium chlorate is an endothermic compound, $\text{KClO}_3 = \text{KCl} + \text{O}_3$ (liberated) + 11.9 cal. It develops 33.5 litres of oxygen for 1 grm. However, potassium chlorate is not classed among explosive bodies, since it does not detonate under a progressive heating. The author makes a series of experiments on the conditions which cause this substance to detonate, and compares them with the conditions under which picric acid explodes.

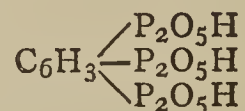
Researches on and Estimation of very Small Quantities of Arsenic in Tissues.—Armand Gautier.—The author's method consists in destroying the organic matter successively by nitric acid and sulphuric acid, then again by nitric acid. The action from the beginning to the end takes place in the midst of strongly oxidising agents, and the whole of the chlorides are destroyed almost at the beginning, these latter being one of the principal causes of the loss of arsenic under the form of volatile compounds.

Dissociation by means of Water, of Ammonium Iodomercurate and Potassium Iodomercurate.—Maurice François.—The author's series of experiments show that the decomposition of ammonium iodomercurate, $\text{HgI}_2\text{NH}_4\text{I} \cdot \text{H}_2\text{O}$, by small quantities of water, is limited and reversible. It obeys the laws of the dissociation of salts by water. The same is true of the decomposition of potassium iodomercurate, $\text{HgI}_2\text{KI} \cdot 5\text{H}_2\text{O}$. When the state of equilibrium is reached, the liquor contains a quantity of free NH_4I and KI , constant for a given temperature.

Heat of Fractionated Neutralisation of Carbonyl Ferrocyanhydric Acid, compared with that of Ferrocyanhydric Acid.—J. A. Muller.—The calorimetric determinations which the author makes lead to the following conclusions:—(1). Carbonyl ferrocyanhydric acid is a strong acid, in the same way as ferrocyanhydric acid, because the neutralisation of these acids by strong bases liberates, in very dilute solutions and at ordinary temperatures, about 14 calories per grm.-atom of hydrogen neutralised. (2). The heat evolved, per grm.-atom of hydrogen, in the neutralisation of carbonyl ferrocyanhydric acid by potash or by baryta, being the same, or sensibly so, as that obtained with ferrocyanhydric acid under the same conditions, it results that the substitution

in the molecule of this latter acid of a divalent CNH group by carbonyl has no sensible influence on the acid energy of the hydrogen atoms which remain in the molecule of carbonyl ferrocyanhydric acid formed.

Some New Compounds of Phosphoric Anhydride and Benzene.—H. Giran.—When benzene monodimeta-phosphoric acid is treated with solutions of soda, potash, ammonia, carbonates of sodium, potassium, &c., yellow precipitates are formed which decompose rapidly under the influence of water. These precipitates are, without doubt, the benzene monodimeta-phosphates of sodium, potassium, ammonium, &c., but it is impossible to collect them. The author has, however, prepared benzene tri-dimeta-phosphoric acid, which has the constitutional formula—



from which the ammonium salt was prepared. He has also established the fact that toluene, xylene, anthracene, and other analogous carbides, unite with phosphoric acid, some even in the cold, to give compounds which appear to be of the same species as the preceding, but which will be examined further.

Preparation of Tetrachlorated and Tetrabromated Orthoquinones from corresponding Halogenated Gaïacols and Veratrols.—H. Cousin.—The result of the author's experiments on the preparation of the above compounds shows that nitric acid first saponifies the tetrachlorated and tetrabromated gaïacols and veratrols, and transforms them into substituted pyrocatechins. These are then oxidised, and give the corresponding quinones.

No. 24, December 11, 1899.

A General Method for the Estimation of some Simple Bodies contained in Organic Compounds.—M. Berthelot.—The author shows that it is possible to use a general method for estimation of simple bodies, easier and more rapid in many cases than the ordinary method, founded on the same principles as those employed for calorimetric investigations. A short account is given of the results observed in the analyses which follow the calorimetric determination. Oxygen is used compressed to 25 atmospheres in a calorimetric bomb. Carbon is thus weighed in the form of CO_2 , hydrogen as water. &c.

Action of Aluminium Chloride on Camphoric Anhydride.—G. Blanc.—The action of aluminium chloride on camphoric anhydride gives, as is known already, isolaunonic acid. At the same time, during this reaction, are produced a certain number of secondary products. After the separation of isolaunonic acid, the mother-liquor is subjected to distillation under reduced pressure, when it is separated into two parts, a portion which distils over and a residue. A number of extractions with potassium bicarbonate divide the distillate into two parts, one acid and one neutral. The acid portion consists probably of a mixture of the two substances corresponding to the formulæ $\text{C}_9\text{H}_{14}\text{O}_2$ and $\text{C}_9\text{H}_{16}\text{O}_2$. The neutral portion of the distillate is composed of an oily liquid, which is most probably the lactone of an acid, $\text{C}_9\text{H}_{16}\text{O}_3$.

Alkalimetry of Amines.—A. Astruc.—The author has examined successively the alkalimetric titration of fatty and aromatic amines, using methyl orange and phenolphthalein as indicators. The two reagents employed successively enable two very different basicities to be characterised; that of the purely fatty amines, which behave as strong bases, giving results in accordance with the thermochemical numbers; those of the primary aromatic amines behave as very feeble bases, only affecting methyl orange, a result which is also in accordance with thermochemical numbers. The influence of a second aromatic radicle in a secondary aromatic amine is to make the basicity entirely disappear to both indicators.

MISCELLANEOUS

International Congress of Methods of Testing Building Materials.—It has been decided to hold an International Congress on the Methods of Testing Building Materials, in connection with the forthcoming Paris Exhibition, from July 9 to 16, 1900, in Paris. Any one desirous of attending this Congress can obtain all information from the Secretary at the Exhibition Buildings.

MEETINGS FOR THE WEEK.

TUESDAY, Jan. 2nd. } Royal Institution, 3. (Christmas Lectures to
THURSDAY, 4th. } Young People). "On Fluids in Motion and
SATURDAY, 6th. } at Rest," by Charles Vernon Boys, F.R.S.
TUESDAY, 9th. } (Experimentally illustrated).

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